Doctoral Thesis

From High-value to Byproduct and Waste Materials for Thermochemical Energy and CO_2 Storage

Carried out for the purpose of obtaining the degree of Doctor technicae (Dr. techn.)
submitted at TU Wien, Faculty of Mechanical and Industrial Engineering

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Affidavit

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such.

I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

Vienna, December, 2019

Signature

Abbreviations

BET	Brunauer–Emmett–Teller (surface area)
CCS	carbon capture and storage
CSP	concentrated solar power
DSC	differential scanning calorimetry
EN	European standard
FLUWA	saure Flugaschenwäsche
FLUREC	Flugasche-Recycling
HFCs	hydrofluorocarbons
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICPP	Intergovernmental Panel on Climate Change
IEA	International Energy Agency
LHS	latent heat storage
LOQ	limit of quantification
MSW	municipal solid waste
MSWI	municipal solid waste incinerator
NPK	non-parametric kinetics
PCMs	phase change materials
PFCs	perfluorocarbons
ppm	part per million
PSD	particle size distribution
RF	radiative forcing
SEM	scanning electron microscope
SHS	sensible heat storage
STA	simultaneous thermal analysis
TCES	thermochemical energy storage
TES	thermal energy storage
TGA	thermogravimetric analysis
XRF	X-ray fluorescence
XRD	X-ray diffraction

Contents

Acknowledgments

Apart from my personal efforts and willingness to achieve high academic education, there have been people who have contributed to this achievement, and I would like to take the opportunity to express my gratitude to those persons.

First of all, I thank Prof. Franz Winter for giving me the opportunity to conduct my PhD on a futuristic and interesting topic such as thermochemical energy storage and all his trust, support, and supervision during these years.

I also want to thank Prof. Andreas Werner for his support and guidance when it was necessary.

My greatest appreciation and thanks go to my father Sourosh Setoodeh Jahromy and mother Parvin Heidari, who have always been supportive and have encouraged me to pursue high academic education since childhood.

I thank Aunt Farah Heidari and my brother Dipl.-Ing. Sepehr Setoodeh Jahromy and other family members for their contributions and continuous support.

Last, but not least, I thank my wife Dr. Fatmeh Albekord for all her permanent support and for enriching my life beyond the university.

Abstract

Population increase, our dependency on fossil energy sources, massive urbanization, our managing system of energy sources, lack of economical technologies, and our tendency to have a more comfortable life have all contributed to the change in climate, which has already altered biological life on Earth.

To mitigate the trend of climate change, fast, serious, and correct global decisions at the political level are needed, in particular for shifting to renewable energy sources, before the global temperature rise increases by 2 °C, above which climate change will be an irreversible process, resulting in considerable danger for human life on Earth.

Renewable energy sources fluctuate in time, particularly solar energy. Therefore, storing energy in the time when the sun is available is necessary for developing concentrated solar power (CSP) plants as sustainable energy suppliers and to compete against fossil-fuel energy sources. Thermochemical energy storage (TCES) as a modern technology, which is still under development, can contribute to bridge the gap between supply and demand by storing the excess heat from CSP plants or any other plant in chemical components through endothermic chemical reactions and releasing the stored heat when energy is needed. Storing energy is the key element for accelerating the shift to renewable energy sources.

The CuO/Cu_2O system is a potential TCES candidate for use in CSP; however, there are still unsolved challenges and knowledge of this system that require more investigations to accelerate its implementation on the industrial scale. The kinetics of this system have not gained enough attention. Furthermore, the knowledge about the kinetics for scaling up this system is vital. Therefore, investigations have been performed to identify the kinetics triplet (model, activation energy, and frequency factor) and the impact of partial pressure on the oxidation kinetics (releasing energy). Kinetics evaluations have been performed by the non-parametric kinetics (NPK) method.

Another existing challenge for industrial implementation of TCES is the cost of chemicals. The focus of research regarding suitable materials for TCES lies on raw or doped material. In the frame work of this thesis, the potential of fly ash as a byproduct or waste from different industries such as paper and pulp, biomass, and municipal solid waste (MSW), whose cost is low or almost minimal, were investigated.

Owing to reaction of alkali metal oxides such as CaO in fly ash with CO_2, the CO_2 storage capacity of reactive fly ash with carbon dioxide in the dry and wet carbonation process in simultaneous thermal analysis (STA) was evaluated. The investigation performed within this thesis shows that some fly ash samples can be considered as TCES and carbon capture and storage (CCS) materials. In addition, different system integrations are presented for future studies and evaluation.

The results of this thesis will allow the inclusion of byproducts or waste from industries in the search spectrum for TCES and CCS materials, resulting in the acceleration of the industrial implementation of TCES, thus making TCES more sustainable and affordable from the ecological and economical viewpoint.

Kurzzusammenfassung

Das Anwachsen der Bevölkerung, unsere Abhängigkeit von fossilen Energieträgern, Urbanisierung, unser Managementsystem der Energie und unsere Tendenz zu einem angenehmen Leben haben alle dazu geführt, dass das Klima unserer Erde sich ändert.

Um den Trend des Klimawandels einzudämmen, sind schnelle, ernsthafte und korrekte globale Entscheidungen auf politischer Ebene erforderlich. Insbesondere die Umstellung auf erneuerbare Energiequellen, bevor der globale Temperaturanstieg größer als 2 °C ist, wodurch der Klimawandel ein irreversibler Prozess wird. Dies bringt eine erhebliche Gefahr für das menschliche Leben auf der Erde mit sich.

Erneuerbare Energiequellen schwanken mit der Zeit, wie die Sonnenenergie. Die Speicherung von Energie in der Zeit, in der die Sonne zur Verfügung steht, ist daher notwendig, um Solarkraftwerke als nachhaltige Energielieferanten zu bewerten. Der thermochemische Energiespeicher (TCES) als eine moderne Technologie kann dazu beitragen die Lücke zwischen Angebot und Nachfrage zu schließen. Die überschüssige Wärme von konzentrierenden Solaranlagen (concentrated solar power, CSP) oder anderen Anlagen können in chemischen Komponenten durch endotherme chemische Reaktionen gespeichert und bei Bedarf die gespeicherte Wärme durch exotherme chemische Reaktionen freigesetzt werden.

Das CuO/Cu_2O System ist ein potenzieller TCES-Kandidat für die Verwendung in CSP. Es gibt jedoch immer noch Herausforderungen dieses Systems, welche weitere Untersuchungen erfordern, um seine Implementierung im industriellen Maßstab zu ermöglichen. Die Kinetik dieses Systems für die TCES wurde nicht genügend untersucht, was für die Skalierung dieses System von entscheidender Bedeutung ist. Daher wurden im Rahmen dieser Arbeit Untersuchungen durchgeführt, um die kinetischen Daten (Modell, Aktivierungsenergie und Frequenzfaktor) und den Einfluss des Partialdruckes auf die Oxidationskinetik (Freisetzung der Energie) zu identifizieren. Die Auswertung der Kinetik-Daten wurde mittels einer modelfreien Methode Namens „non-parametric kinetics (NPK)“ durchgeführt.

Eine weitere derzeit bestehende Herausforderung für die industrielle Implementierung der TCES sind die hohen Kosten der Chemikalien. Der Fokus der Forschung liegt derzeit an Rohstoffen oder dotierten Materialien. Ein Material, das alle TCES-Anforderungen aus technischen, ökologischen und wirtschaftlichen Gesichtspunkten erfüllt, ist noch nicht verfügbar. Nach unserem besten Wissen, wurde das Potential der Abfälle bzw. Nebenprodukte der Industrie noch nicht in die Richtung TCES untersucht. Daher wurden im Rahmen dieser Arbeit die Flugascheproben, die bei der Verbrennung von Siedlungsabfällen (MSWI), Biomasse und Abfälle der Papier- und Zellstoffindustrie entstehen zum Ziel der Evaluierung Ihres Potentials als TCES und CO_2 Speicher untersucht. Darüber hinaus werden verschiedene Systemintegrationen für zukünftige Studien und Bewertungen vorgestellt.

Die Ergebnisse dieser Dissertation ermöglichen die Aufnahme von Nebenprodukten oder Abfällen aus der Industrie in das Suchspektrum nach TCES- und CCS-Materialen. Dies beschleunigt die industrielle Umsetzung von TCES und macht TCES unter ökologischen und ökonomischen Gesichtspunkten nachhaltig.

List of Papers included in the Thesis

Setoodeh Jahromy, S.*; Birkelbach, F.; Jordan, 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**. *Energies* 2019, 12(3), 508.

Setoodeh Jahromy, S.*; Jordan, C.; Azam, M.; Werner, A.; Harasek, M.; Winter, F. **Fly Ash from Municipal Solid Waste Incineration as a Potential Thermochemical Energy Storage Material**. *Energy Fuels* 2019, 33, 7, 5810-5819.

Setoodeh Jahromy, S.*; Azam, M.; Huber, F.; Jordan, C.; Wesenauer, F.; Huber, C.; Naghdi, S.; Schwendtner, K.; Neuwirth, E.; Laminger, T.; Eder, D.; Harasek, M.; Winter, F. **Comparing Fly Ash Samples from Different Types of Incinerators for Their Potential as Storage Materials for Thermochemical Energy and CO_2.** *Materials 2019*, 12(20), 3358.

List of Papers not included in the Thesis

Huber, C.; Setoodeh Jahromy, S.; Jordan, C.; Schreiner, M.; Harasek, M.; Werner, A.; Winter, F. **Boric Acid: A High Potential Candidate for Thermochemical Energy Storage.** *Energies* 2019, 12(6), 1086.

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Azam, M., Setoodeh Jahromy, S.; Waseem, R.; Jordan, C.; Harasek, M.; Winter, F. **Comparison of the Combustion Characteristics and Kinetic Study of Coal, Municipal Solid Waste and Refuse-Derived Fuel**: **Model-Fitting Methods**, *Energy Science & Engineering* 2019;00:1-12.

Azam, M.; Setoodeh Jahromy, S.; Raza, W.; Raza, N.; Lee, S.S.; Kim, K.-H.; Winter, F.; **Status, characterization, and potential utilization of municipal solid waste as renewable energy source: Lahore case study in Pakistan**, *Environment International* 2020, 134, 105291.

Poster, Conference and book contributions

Mudasser Azam, Saman Setoodeh Jahromy, Franz Winter
Municipal Solid Waste Management in Lahore, Pakistan: Characterization & Energy Content
Recy&DepoTech 2018, 7.-9. November 2018, Leoben, Austria

Saman Setoodeh Jahromy*, Felix Birkelbach, Andreas Werner, Franz Winter
Partial Pressure Impact on the Reactions of CuO/Cu_2O & Co_3O_4/CoO for Thermochemical Energy Storage (TCES)
Jahrestereffen der ProcessNet-Fachgruppe Energieverfahrenstechnik, 6.-8.März 2018, Frankfurt am Main, Germany

Saman Setoodeh Jahromy*, Christian Jordan, Andreas Werner, Michael Harasek, Franz Winter
Fly Ash as Thermochemical Energy Storage Material
Jahrestereffen der ProcessNet-Fachgruppe Energieverfahrenstechnik, 5.-7.März 2019, Frankfurt am Main, Germany

Saman Setoodeh Jahromy*, Franz Winter
Characterization of Solid Fuels (FRU)
9. Österreichisches IEA-Wirbelschichttreffen, 26.-28. April 2017, Bad Blumau, Austria

Saman Setoodeh Jahromy*, Christian Jordan, Michael Harasek, Franz Winter
Advanced Application of Fly Ash
10. Österreichisches IEA-Wirbelschichttreffen, 11.-13. April 2018, Erlebnis Welt Energie, Timelkam, Austria

Saman Setoodeh Jahromy*, Christian Jordan, Mudassar Azam, Andreas Werner, Michael Harasek, Franz Winter
Fly Ash as Thermochemical and CO_2 Storage Material
11. Österreichisches IEA-Wirbelschichttreffen, 3.-5. April 2019, Bruck an der Mur, Austria

Saman Setoodeh Jahromy*, Christian Jordan, Mudassar Azam, Andreas Werner, Michael Harasek, Franz Winter
Fly Ash from Municipal Solid Waste Incineration as a Potential Thermochemical Energy Storage Material
The 27th International Conference on the Impact of Fuel Quality on Power Production and the Environment, September 24th – 28th, 2018 Lake Louise, AB, Canada

Saman Setoodeh Jahromy*, Christian Jordan, Michael Harasek, Franz Winter
Flugasche als Thermochemischer Energie- und CO_2-Speicher
Berliner Konferenz-Mineralische Nebenprodukte und Abfälle, 13. und 14. Mai 2019, Berlin, Germany

Saman Setoodeh Jahromy*, Franz Winter
Potential of Fly Ash as Thermochemical Energy and CO_2 Storage Material
18. Österreichische Chemietage 2019, September 24.-27, 2019, Linz/Austria

Saman Setoodeh Jahromy*, Christian Jordan, Michael Harasek, Franz Winter
Fly Ash as Thermochemical Energy and CO_2 Storage
IRRC-Waste-To-Energy, October 14 and 15, 2019, Vienna, Austria

Saman Setoodeh Jahromy*, Franz Winter
Fly Ash Utilization
IEA-FBC, October 17 and 18, 2019, Vienna, Austria

1 Introduction

Nowadays, humans are facing a global challenge which is a threat to human life everywhere on our planet. This challenge is called “climate change.”

Most of the reasons of climate change are created by humans through anthropogenic activities. Population increase, our dependency on fossil energy sources, massive urbanization, our managing system of energy sources, lack of technologies, and our tendency to have a comfortable life have contributed to the changes in our climate, which will subsequently change our life.

The climate of our planet has been changing since historical times. Some changes have created life and some have destroyed it, and the climate today is a product of all changes that our planet has faced. Nonetheless, the differences in today’s climate change are the greenhouse gases emitted by humans that have made our planet experience global warming, which has not happened in the history of our planet in the last 800,000 years [1].

Carbon dioxide (CO_2) along with water vapor, methane, nitrous oxide, and halogen carbon compounds is one of the main greenhouse gases that impacts global warming. The concentrations of all greenhouse gases except water vapor in comparison with CO_2 concentration are less in the atmosphere; however, their impacts on global warming are higher than those of CO_2. Nonetheless, the life time and produced amount of CO_2 is higher than those of other greenhouse gases. Despite the water vapor cycle (evaporation, condensation/rain), carbon dioxide remains in the gas phase in the atmosphere for hundreds and even thousands of years. Based on an Intergovernmental Panel on Climate Change (IPCC) report, CO_2 has the highest radiative forcing (RF/expressed as watt per square meter) in the time period between 1750 and 2011 when compared with that of other greenhouse gases (methane, halocarbons, and nitrous oxide), aerosols, and other precursors [2]. All these issues have made CO_2 the most important contributor to climate change, resulting in global warming.

Carbon dioxide (CO_2) is a naturally generated gas molecule in the Earth’s atmosphere. It has biological, geological, and anthropogenic sources. Based on the results of ice cores, the CO_2 concentration in the atmosphere has varied between 190 ppm and 280 ppm in the last 420 000 years. To date, the concentration of carbon dioxide has reached above 412 ppm [3].

The effect of greenhouse gases was first discovered by Furrier in 1816, and later, Claude Pouillet speculated that CO_2 and water vapor absorb infrared radiation, resulting in global warming [4,5]. The first experimental evidence was provided by Eunice Foote in 1986 and three years later by John Tyndall [6-8]. Next, in 1896, Arrhenius calculated the effect of doubling the CO_2 concentration on the temperature increase [4,9]. Nonetheless, the term greenhouse was not used by the above mentioned scientists. The term greenhouse was first used by Swedish meteorologist Nils Gustaf Ekholm [10]. In the last century, CO_2 concentration was measured and modeled by Keeling, known as the Keeling curve [11]. All findings and attempts of scientists around the globe have described the CO_2 concentration today in the atmosphere well. Global warming as a result of greenhouse gases, particularly CO_2, is gaining the attention of everyone everywhere. Catastrophes that occurred once per century are occurring often.

Now, we as humans have duties and the chance to change the trend of global warming generated by us before it becomes irreversible.

In this regard, in 1997, the Kyoto protocol was developed as an international agreement with the scope of reducing greenhouse gases, particularly CO_2, CH_4, N_2O, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6), to least 5% below the 1990 levels in the commitment period of 2008 to 2012 [12].

Following the Kyoto Protocol, in December 2015, 195 countries agreed on a universal, legal, and global protocol to maintain global warming below 2 °C to prevent or limit climate changes [13]. Despite the Kyoto protocol, the Paris agreement bonded countries with obligations, and the implementation of those obligations was to be reported after a certain period of time. Moreover, the set target, keeping global warming below 2 °C, is a measurable value for evaluation of the impact of greenhouse gases on the environment. The set target of 2 °C is the threshold for maintaining the reversible station of the environment processes. However, Fischer et al. reported that even with this target, adapting to new conditions on Earth should be expected [14]. Nonetheless, to achieve the set target, humans are responsible to take actions. Industries need to take particular action because most CO_2 is emitted in the atmosphere from the energy sector based on IPCC reports [1,15]. Thus, Industries have to alter their processes.

The methods that can make this possible for industries are as follows:

- shift to renewable and sustainable energy sources;
- store and utilize CO_2;
- increase the efficiency of plants; and
- store surplus energy or waste energy for further use.

Renewable energy sources such as concentrated solar power (CSP) 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 energy for further use. Thermal energy storage involves three methods: sensible heat storage, latent heat storage, and thermochemical energy storage (TCES). Sensible and latent heat storages are state-of-the-art techniques. But TCES is under development.

Carbon capture and storage (CCS) can play an essential role in decreasing CO_2 from industries and even directly from the air, leading to negative emissions [16]. “Despite its technical maturity, CCS has not been deployed on the scale understood to be required, due to various technical, commercial and economic challenges” [16]. CCS is defined as the capture of CO_2, followed by transport and storage in geological reservoirs or oceans [17]. CCS includes three processes: pre-combustion, post-combustion, and oxy-fuel processes [16]. In the oxy-fuel process, oxygen is used instead of air for combustion, resulting in rich CO_2 exhaust gas with water vapor. In the pre-combustion process, the fuel is first partially oxidized, and the generated syn-gas (CO and H_2) in the gasifier reacts with steam to produce more rich-hydrogen gas (H_2) and CO_2. In the post combustion process, liquid or solid materials are used to separate the generated CO_2 after combustion. Separation can be performed by different techniques such as adsorption, absorption, membrane separation, and cryogenic techniques and through micro algal bio-fixation [17].

Some solid materials are based on natural minerals such as olivine and serpentine or synthetized materials such as zeolites, silica gel, activated carbons, carbon fibers, ion exchange resins, and metal oxides (CaO, MgO, K_2O, and Li_2O) [17]. Fly ash generated from coal is another solid adsorbent for CO_2 [18]. Nonetheless, the search for materials is still continuing and under development. Therefore, this thesis investigates fly ashes from MSW, biomass, and paper and pulp industries for their potential as CCS material. In Austria, around 440 000 t/y fly ash is produced from different industrial sectors [19].

1.1 Sensible Heat Storage (SHS)

Sensible energy storage is the simplest type of heat storage system. Surplus heat or waste heat can be used to increase the temperature of a material such as water or SiO_2 to a certain level without any changes in phase of the material. Materials with high heat capacity are used, such as water, sand, concrete, silicon oil, or nitrite salts [20]. The disadvantage of this type of heat storage is the duration for storage. Insulation of the material is possible; however, it leads to high cost. SHS is a state-of-the-art technique of thermal energy storage for CSP.

1.2 Latent Heat Storage (LHS)

Latent heat storage uses the heat capacity and phase change enthalpy of a material to store and release heat. Because of the use of phase change of materials for storing and releasing heat, these materials are known as phase change materials (PCMs). Salts such as sodium or potassium salts or their mixtures, other salts, alloys, metals, and paraffines as organic PMCs for lower temperature (< 200 °C) are the most used LHS materials [21]. Compared with SHS, the energy density of LHS is higher. However, at the same time, the operational cost is higher because of corrosion, low thermal conductivity, separation between phases, and the requirement of temperature to be maintained above the melting point to avoid phase change and upper temperature limitation [21,22]. There are commercially available PCMs. However, the search and development for PCMs are still continuing.

1.3 Thermochemical Energy Storage (TCES)

TCES is a modern technique that uses the enthalpy of chemical reactions to store and release heat.

Compared with SHS and LHS, this technique is less developed. However, TCES is a futuristic method for storing excess heat owing to the high energy density, the ability to store heat for long periods of time over seasons, and easy transport [23].

When surplus energy from any plant is available, TCES can be used to run endothermic reactions. For instance, material $A_{(s)}$ decomposes into its products $B_{(s)}$ and $C_{(g)}$ through an endothermic reaction. Therefore, thermal heat is stored in material $B_{(s)}$. When heat is required, material $B_{(s)}$ can react with gaseous $C_{(g)}$ to form the initial component $A_{(s)}$ through an exothermic reaction. Figure 1 illustrates the principle of TCES systems [24].

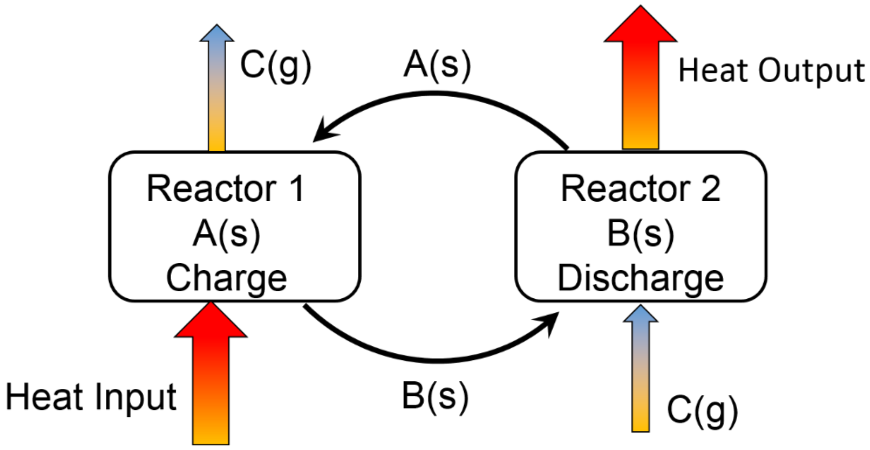

Figure 1. Concept of TCES

Solid-gas reactions due to the easy separation between gas and solids are preferable. However, TECS is not restricted just to gas-solid reaction systems.

In the ancient years in Persia, Razi cooked eggs by heating the water with CaO [25]. This may be one of the first documented use of chemical heat energy in which heat is released through exothermic chemical reaction of CaO with water to build calcium hydroxide [26].

In 1961, Goldstein in the Conference of United Nation on new Sources of Energy in Rome suggested the use of chemical reactions for storing heat in chemicals and offered some chemicals for this purpose [27]. The thermochemical cycle for storage of energy was then introduced and summarized by Funk and Reinstrom in 1966 and later by Ervin in 1977 [28]. The focus of research from the beginning was on raw materials. However, raw materials have some drawbacks, which have been attempted to overcome by doping or mixing them with other THS or TCES materials [29,30]. To the best of my knowledge, waste or byproducts from industries, which may have good or optimal properties for use as TCES materials, have not been investigated so far. The chemical composition, the produced amount of fly ash, and less or no cost leading to monetary benefits for fly ash such MSW fly ash from the industry make it an interesting product to investigate its potential as TCES materials [23].

1.4 Carbon Capture and Storage (CCS) Materials

There are materials in solid and liquid forms that can capture CO_2. Among the various aqueous, amines are the most efficient liquid used in industries for the purpose of CO_2 capture [31]. Water is another solution that can capture CO_2, and therefore, oceans are considered to be CO_2 capture entities. However, this has led to the acidification of ocean water, which subsequently has impacted microorganism life.

Natural or synthetized zeolites and activated carbon known as solid materials can capture CO_2. Lava stone and other minerals such olivine and serpentine are also as CO_2 capture materials. Active coke is the most used solid adsorbent material in industries because of the less energy required for regeneration, low cost, and high surface area resulting in high capacity [17].

Different approaches for using fly ash generated from coal power plants as CO_2 storage materials or to enhance properties of fly ash through carbonation for further use as an admixture in construction materials have already been developed worldwide [18,22]. The carbonation of fly ash from other industries particularly from MSW has not gained much attention as much as coal fly ash owing to the development of MSW incinerators and categorization of fly ash from MSW as hazardous material in most countries, thus leading to its disposal after a stabilization process or its underground landfilling. Calcium oxide (CaO), as mentioned before, along with aluminum oxide and silicon oxide is one of the main components of fly ash generated from MSW, biomass, and paper and pulp industries. According to XRF analysis performed for fly ash samples within this thesis, the calcium oxide (CaO) content in fly ash samples varies in the range of 15%–65%. Calcium oxide (CaO) in fly ash can react with CO_2 to calcite ($CaCO_3$) through an exothermic reaction (see Eq. 1).

$$CaO_{(s)} + CO_{2\,(g)} \leftrightarrows CaCO_{2\,(s)} + \Delta H_R \qquad \text{(Eq. 1)}$$

This feature of CaO could make the fly ash to be considered as CO_2 storage material.

2 Objective and Structure of the Thesis

One of the objectives of this thesis was to investigate the kinetics of CuO/Cu_2O as one of the high-value and potential candidates in the field of TCES. Knowledge of the kinetic parameters of any reaction is essential for the scale up of any system.

However, the main objective of this thesis is to evaluate the potential of waste and byproducts, particularly fly ash, from different industries for their potential as thermochemical energy and CO_2 storage materials.

In this thesis, three papers are included. In the first paper, the kinetics of the CuO/Cu_2O system as a suitable TCES material are evaluated with modern non-parametric kinetics (NPK). The kinetics (model, activation energy, and frequency factor) were determined, and the impact of distance to equilibrium was integrated in the pressure term.

In the second paper, the potential of three fly ashes generated from three different grate furnaces in Austria for their potential as TCES materials was evaluated.

In the third paper, the potential of six fly ashes from six different MSW plants (grate furnaces, fluidized bed, and rotary kiln) for CO_2 and TCES was obtained.

In addition, other important and relevant results from the evaluation of carbonation of fly ash samples and different system integrations are presented and discussed in this work.

3 Materials and Methods

For the chemical and physical analysis of materials, the following equipment was used:

This part is taken from materials and methods included in papers I, II, and III:

Table 1 shows the selected fly ash samples for the analysis.

Table 1. Fly ash samples, technologies used and fuel types presented in this work

Fly ash sample	Technology	Fuel Type
Fly ash A	Grate furnace	MSW
Fly ash B	Grate furnace	MSW
Fly ash C-boiler	Grate furnace	MSW
Fly ash C-filter	Grate furnace	MSW
Fly ash D	Rotary kiln	Hazardous waste
Fly ash E	Fluidized bed	MSW
Fly ash F	Fluidized bed	Residues from paper and pulp
Fly ash G	Fluidized bed	Biomass

3.1 PSD Analysis

Particle size distribution was measured using a laser diffraction analyzer (Mastersizer 2000, Malvern Panalytical) using a red helium-neon-light source at 633 nm and a blue light source at 466 nm. With this setup, it was possible to measure particle size in 50 different classes from 0.02 µm up to 2000 µm. All samples analyzed in this study were dry dispersed at 2 bar injector air pressure. A sample mass between 2 g and 10 g was placed on the vibrating gutter, and for each sample, at least 6 measurements were performed to obtain an average value.

3.2 BET Analysis

Specific surface measurements were performed by physisorption (ASAP 2020, Micromeritics GmbH) according to Brunauer–Emmett–Teller (BET) analysis. The gas used was N_2, and the analysis bath temperature was -195 °C. To eliminate adsorbed gases and moisture from the sample, the sample was heated up to 120 °C under vacuum overnight. The sample masses were between 0.2 and 0.8 g.

3.3 SEM Analysis

The FEI Quanta 250 FEGSEM (FEI, USA) was used for scanning electron microscope (SEM) pictures. The pictures were recorded at 3 kV and 5 kV acceleration voltage under high vacuum of 6.10^{-6} mbar. A magnification of 500 and 1000 for fly ash samples and 10,000 for CuO samples was applied to illustrate the thermal treatment of samples after STA runs.

3.4 XRF Analysis

A wavelength-dispersive X-ray spectrometer (Axios, Panalytical) was used for X-ray fluorescence (XRF) analysis. The tube was an Rh-A device with an excitation voltage of 50 kV and an electric current of 50 mA. All measurements were carried out in an evacuated sample chamber. Sample preparation was performed by melt-digestion with di-lithium tetraborate, and the sample was mixed with 8 g of di-lithium tetraborate and melted in air in a Pt crucible at 1050 °C. After homogenization, a clear melt was poured in a tablet and analyzed.

3.5 XRD

Powder X-ray diffraction (XRD) measurements were carried out on Panalytical Xpert-Pro diffractometer (CuKα, 45 kV, 40 mA, continuous scan, Soller slits 0.04 rad, Bragg-Brentano HD mirror, X'Celerator detector, 2θ range 5-70° for fly ash samples/5-90° for CuO sample, 200 s/step measurement time, 25 °C). Representative samples were ground manually in an agate mortar for 5-10 minutes and mounted onto a zero-background sample holder with minute amount of grease. Evaluation and phase identification were carried out using the search and match routine of the Panalytical HighScore Plus Program Suite on the ICDD database (ICDD, 2017). This was followed by Rietveld refinement with Topas using CIF-files from the ICSD database for fly ash samples. For the CuO sample, background correction and K_α stripping were performed.

3.6 ICP-OES Analysis

For the analysis of the total content of nonmatrix elements, fly ash samples were digested in aqua regia according to EN 13657 (2002) and subsequently analyzed according to EN 11885 (2009) by inductively coupled plasma optical emission spectroscopy (ICP-OES: PerkinElmer Optima 8300 ICP-OES equipped with a SC-2 DX FAST sample preparation system). A customized single-element standard was used for calibration.

3.7 Simultaneous Thermal Analysis (STA)

Simultaneous thermal analysis (STA) data were generated on a Netzsch STA 449 Jupiter instrument equipped with a TGA-DSC sample holder. This instrument maintained a water vapor furnace, including an air-cooled double jacket, heated vapor inlet, heated transfer line, and a heated collar. The oven had the capacity to operate between 25 °C and 1250 °C by regulation by an S-Type thermocouple. The gas flow rates were controlled using red-y smart (Voegtlin). The purity of gases (CO_2, O_2, and N_2) used was 99.999% (v/v). Aluminum oxide crucibles without lids were used for all experiments. The flow rate of each gas was adjusted in the range of 20 to 100 mL/min for each experimental run.

4 Results and Discussion

4.1 Kinetic Study of Cu_2O/CuO for Use as a TCES Material

The kinetic study of a reaction is necessary for designing a system. The CuO/Cu_2O system is a high potential candidate with high energy density and from the economical viewpoint compared to other metal oxide candidates such as CoO/Co_3O_4 is an interesting system for further investigation. However, there are still unsolved problems with this system such as less knowledge about oxidation kinetics of $Cu_2O_{(s)}$ with $O_{2\,(g)}$ to $CuO_{(s)}$ (Eq 2). Because of the presence of one component in the gas phase, pressure affects the kinetics.

$$2Cu_2O_{(s)} + O_{2\,(g)} \leftrightarrows 4CuO_{(s)} + \Delta H_R \qquad \text{(Eq. 2)}$$

Paper (I) investigated the oxidation kinetics, as illustrated in Figure 2, to determine the kinetics triplet (model, activation energy, and frequency factor). The impact of partial pressure, *h(P)*, was also evaluated by NPK. The NPK method is a modern method used in gas-solid reactions.

To consider the pressure dependency of the reaction, the NPK method was extended at our university. The main benefit of this method is its capability to derive the kinetics model from any combination of experiments without any additional a priori assumptions.

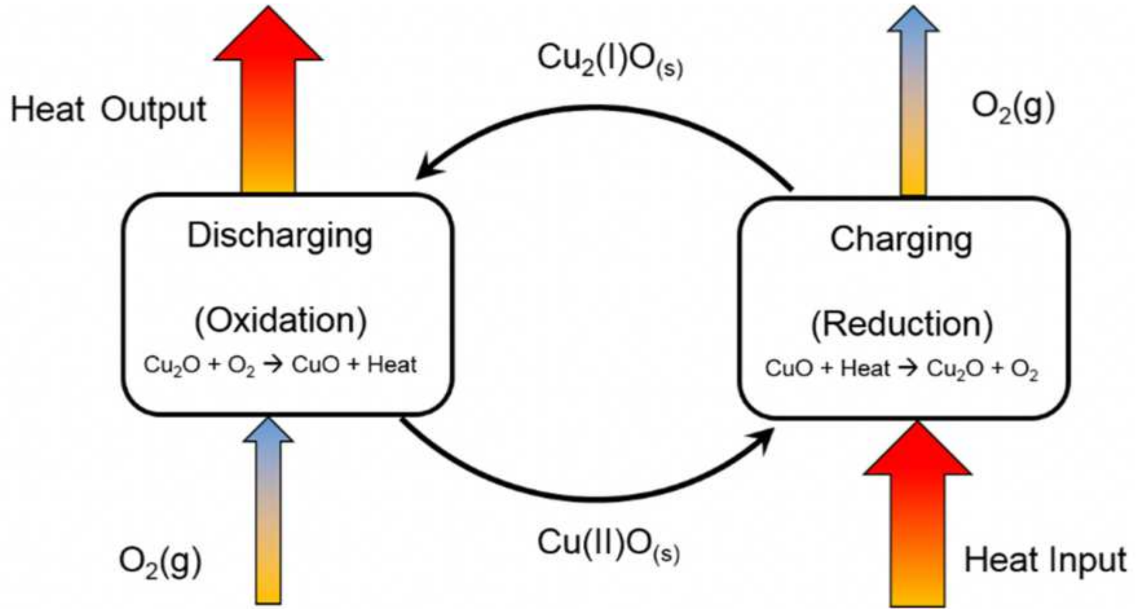

Figure 2. Concept of thermochemical energy storage for Cu_2O/CuO [32]

The equilibrium oxygen pressure for CuO and Cu_2O was generated from thermodynamic data from HSC software and proved experimentally through reduction of CuO to Cu_2O under different oxygen partial pressures in STA. Both results are in good agreement. The results are presented in Figure 3.

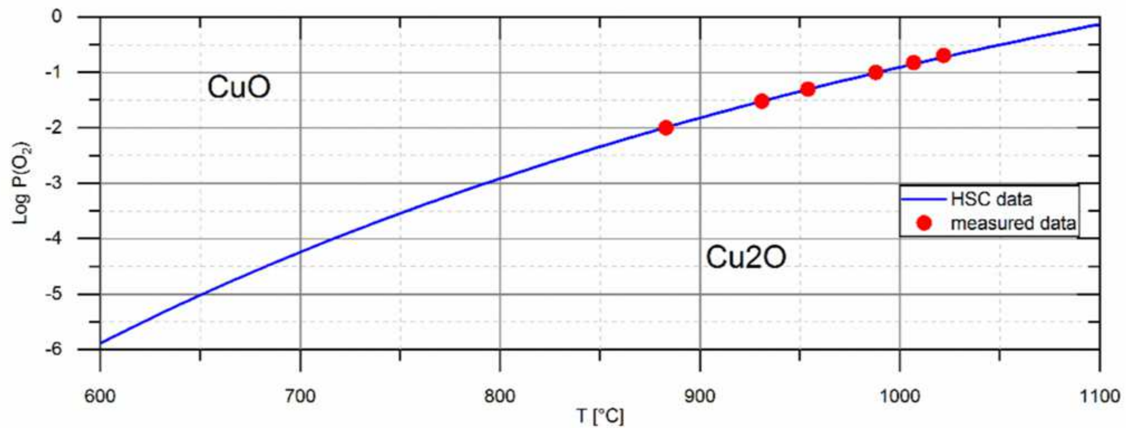

Figure 3. Comparison of the equilibrium oxygen pressure resulting from the HSC database and the experimental data for C_2O/CuO [32].

To determine the oxidation kinetics, four temperature levels and four partial oxygen pressures at each temperature were selected for the experiments. Temperature levels were 800, 830, 870, and 930 °C, and the oxygen partial pressures were 0.1, 0.2, 0.5, and 1 bar. Figure 4 presents the four selected pressure and temperature levels from thermodynamic point for the oxidation reaction of Cu_2O to CuO.

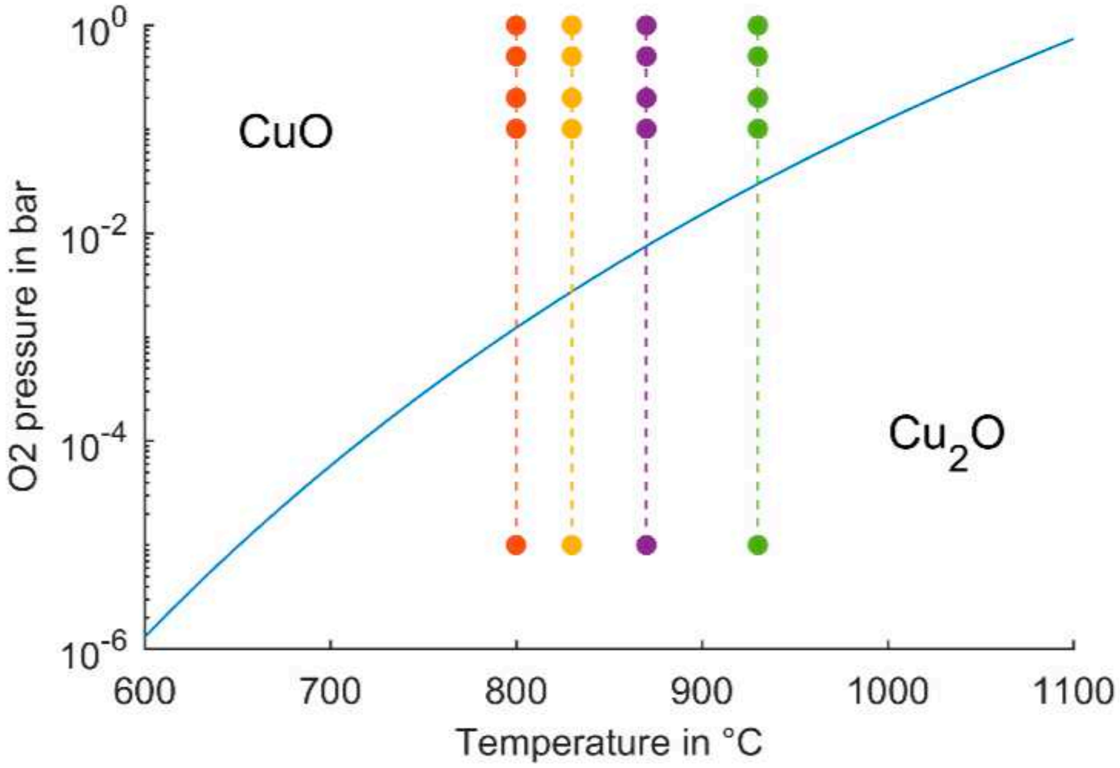

Figure 4. Operation conditions for the measurements relative to the equilibrium curve for the reaction system: Four temperature levels (800, 830, 870, and 930 °C) and four partial pressures (0 bar for reduction and 0.1, 0.2, 0.5, and 1 bar for oxidation) at each temperature were selected for the experiments [32].

To reduce the impact of sample mass on oxidation kinetics, a mass of 8.27 mg was selected for each set of experiments. Conversion and conversion rate oxidation kinetics with at 930 °C and a partial pressure of 0.1 bar of four different masses (50, 10.00, 8.27, and 2.20 mg) were investigated (Figure 5). The results showed that the trend of conversion and conversion rate for masses of 8.27 and 2.20 mg was maintained, and the reason behind selecting the mass of 8.27 mg for this kinetic investigation.

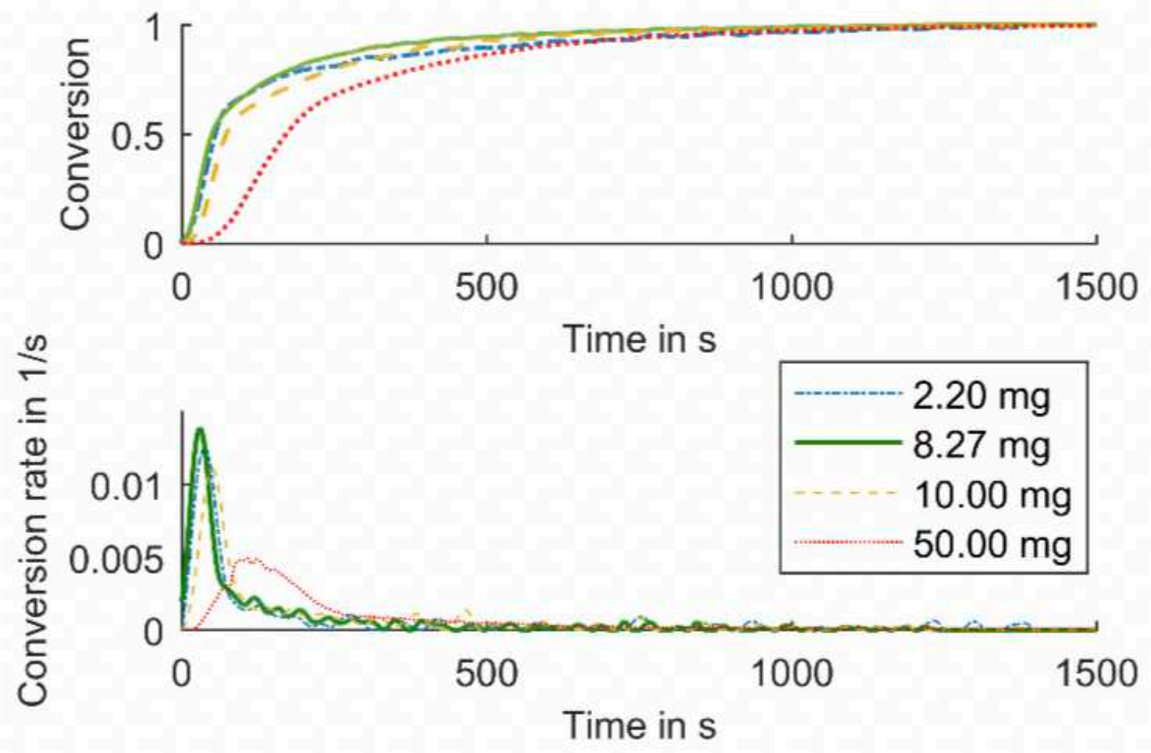

Figure 5. Impact of mass on conversions and conversion rates for the oxidation of Cu_2O at a 0.1 bar oxygen partial pressure and at 93 °C [32].

The kinetic evaluation by NPK showed that the nucleation model, particularly Avrami-Erofeev/A2, is the best fitted model to describe the extent of conversion. The activation energy was 233 kJ/kg with a frequency factor of 5×10^9 1/s.

The pressure term used in the first evaluation was P. The result shows an unusual Arrhenius trend (not an exponential trend) in Figure 6. Therefore, the pressure term was reparametrized from P to 1-P/P* to consider the distance to the equilibrium in the partial pressure term in the general kinetic equitation, which is necessary to match the temperature term to the usual exponential trend of Arrhenius. The result of this reparameterization is shown in Figure 7.

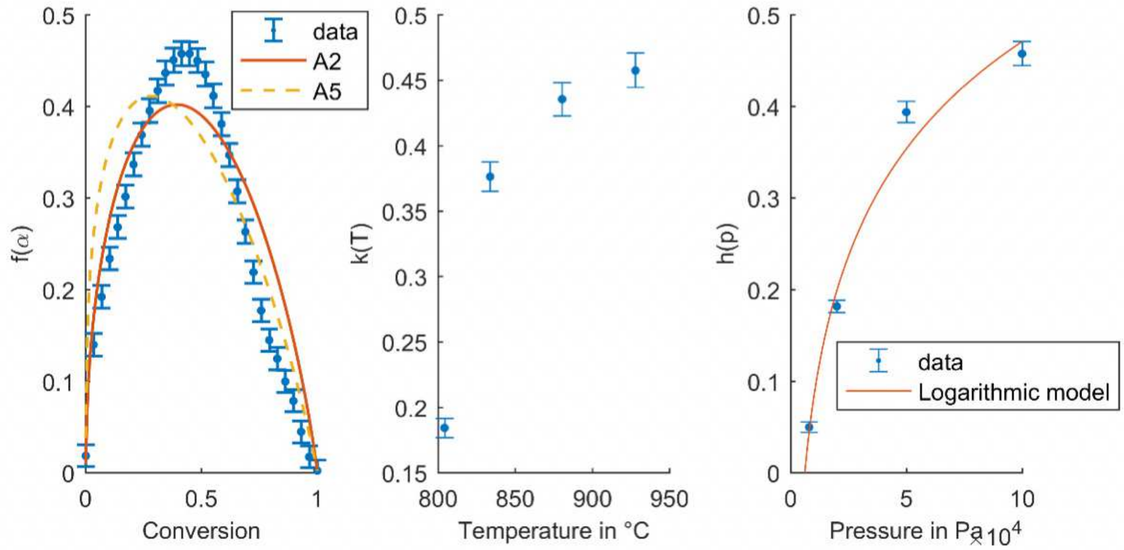

Figure 6. Model generated from all data measured with the NPK method and the best models fitted (A2 and A5) to the experimental data, temperature, and pressure dependencies [32].

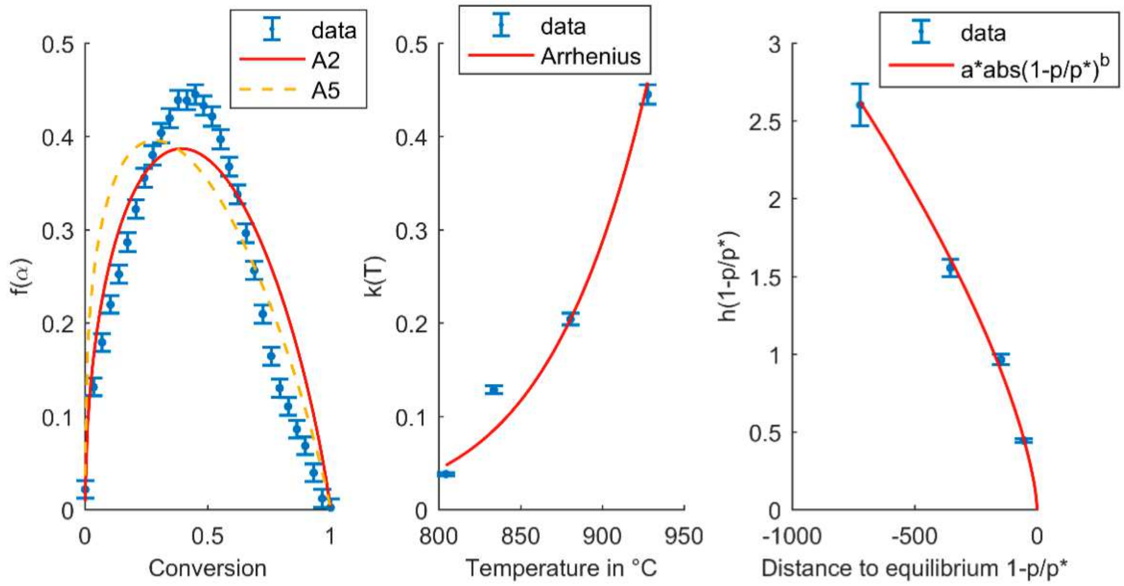

Figure 7. Reparameterization of pressure for considering the distance to the equilibrium curve in the general kinetic equation [32].

Our further investigation showed that the $1-(P/P^*)$ as it is used in literature without further consideration is only valid for decomposition reactions, where the stoichiometric coefficient of the gas phase is 1 [33]. Reading et. al. [34] derived the effect of the reaction equilibrium on the reaction rate based on transition state theory and found that the driving force term is $(1-\exp(G_z/RT)$. Using thermodynamic equations for simple gas-solid reactions with only one gaseous substance, G_z/RT can be substituted by $(p/p^*)^n$. Thus, the stoichiometric factor of the gas component has to be considered. For formation reactions, where the stoichiometric factor is negative, this also prevents large negative values of $1-P/P^*$ in the pressure term. By including the stoichiometric coefficient, a model of Avrami-Erofeev (A2) with an activation energy of 236 kJ/kg and frequency factor of 4.19×10^9 1/s can be obtained (Figure 8).

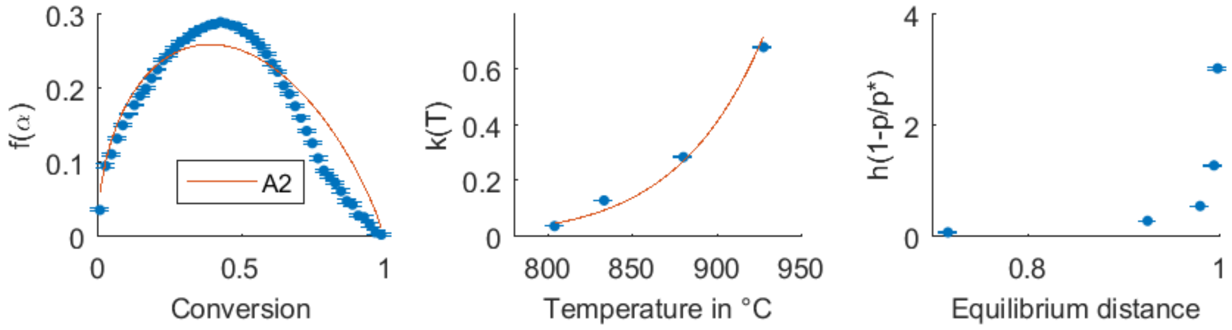

Figure 8. Considering the stoichiometric factor of the gas component (oxygen) in the pressure term [33].

4.2 Fly ash for Use as TCES and CO_2 Storage Material

4.2.1 XRF and ICP-OES

The chemical analysis performed by XRF showed that CaO is one of the main components of each fly ash sample, independent of the origin and combustion technology. The XRF results of fly ash samples from paper II and III are illustrated in Table 2 Table 3. In addition, the XRF results of fly ash F from the paper and pulp industry and fly ash G from the biomass industry are added.

Components that appear in a high amount are silicon oxide (SiO_2), aluminum oxide (Al_2O_3), and metal salts most in the form of sulfates and chlorides. Beside these components, fly ash samples from MSW were rich in heavy metals, which were determined by ICP-OES and are presented in Table 4 for the analyzed fly ash samples. Elements such Zn and Pd can be found in all fly ash samples in high concentrations (Zn > 3800 ppm and Pd > 1100 ppm) compared with other elements. Cu is another element that appears in a concentration over than 1000 ppm in fly ash. In Switzerland, therefore, technologies like as FLUWA and FLUREC have been developed to recover metals like Zn, Pd, Cu, and Cd from fly ash samples [35]. Through FLUREC, Zn with a purity of 99.99% can be recovered from MSW fly ash [36]. However, Fellner et al. studied FLUREC technologies in Austria and reported that with the price for raw Zn, the implementation of this technology for Austria is not applicable owing to the low concentration of Zn in fly ash samples [37]. MSW fly ash is disposed of after stabilization with cement or landfilled in hazardous sites underground in Germany. However, heavy metal concentrations of fly ash make them an interesting source for metal recovery, resulting in source conservation. Nonetheless, economical technologies need to be developed.

The reversible exothermic reactions of CaO with H_2O and with CO_2 to calcium hydroxide ($Ca(OH)_2$) and to calcium carbonate ($CaCO_3$), respectively, allow us to further investigate the potential of fly ash as waste or byproducts from industries for energy and CO_2 storage.

Table 2. Total content of the elements in the mass percent determined by XRF spectroscopy [38,39].

	Fly ash A	Fly ash B	Fly ash C-boiler	Fly ash F	Fly ash G
Na_2O	11.2	10.7	1.9	1.3	2.2
MgO	0.7	0.6	2.7	2.3	6.1
Al_2O_3	6.4	6.9	11.4	11.1	8.3
SiO_2	11.8	13.0	27.4	15.4	33.5
P_2O_5	0.5	0.6	0.7	0.9	2.8
SO_3	8.8	9.9	7.4	1.7	6.0
Cl	14.9	14.1	4.3	0.4	2.9
K_2O	7.5	7.3	2.5	0.4	8.0
CaO	26.6	25.0	32.3	63.5	23.5
TiO_2	1.3	1.3	1.8	0.7	1.3
Fe_2O_3	1	2.6	4.9	1.4	3

Table 3. Total content of matrix elements in fly ash samples determined by XRF and presented as +++++, ++++, +++, ++, and + (very high, high, medium, low, and very low intensities, respectively) [23].

Elements	Fly ash A	Fly ash B	Fly ash C-boiler	Fly ash C-filter	Plant D	Plant E
Na_2O	+++	+++	+	+++	+++	+
MgO	+	+	+	+	+	+
Al_2O_3	++	++	+++	++	+	+++
SiO_2	+++	+++	++++	+++	+++	+++++
P_2O_5	+	+	+	+	+	+
SO_3	++	++	++	++	+++	+
Cl	+++	+++	+	+++	+	+
K_2O	++	++	+	++	+	+
CaO	++++	++++	+++++	++++	+++	++++
TiO_2	+	+	+	+	+	+
Fe_2O_3	+	+	+	+	++	+

Table 4. Total content of nonmatrix elements in different fly ash samples determined by ICP-OES given in mg/kg, where LOQ = limit of quantification [23].

Elements	Plant A	Plant B	Plant C-boiler	Plant C-filter	Plant D	Plant E
Sb	742	635	302	1316	656	127
As	37	32	13	37	83	7
Ba	927	984	1745	1048	183	809
Pb	4883	4394	1100	7016	12948	1254
Cd	347	321	38	375	321	14
Cr	245	259	276	242	780	234
Co	24	27	38	35	111	27
Cu	1008	1004	1009	1901	3315	3608
Mn	574	676	1050	816	816	676
Mo	24	20	22	24	191	10
Ni	59	60	152	95	615	109
Hg	12.50	34.79	0.34	4.34	0.21	<LOQ
Ag	49	44	14	47	126	12
Zn	20722	18371	5684	21613	38108	3870
Sn	948	835	177	865	1154	147

4.2.2 X-ray Diffraction (XRD)

Due to the existence of different crystal structures in fly ash samples, XRD analysis was performed. Results revealed a complex crystal structure mainly including quartz, calcite, sylvite, halite, and anhydrite. Aluminum silicate appears as belite and gehlenite in most cases. Phosphate as whitlockite was identified in fly ash sample D from rotary kiln and E from fluidized bed. The amount of portlandite ($Ca(OH)_2$) found in some samples, in particular in fly ash C-boiler sample, is an alteration product of free lime (CaO). Figure 9 shows the diffractograms of fly ash samples.

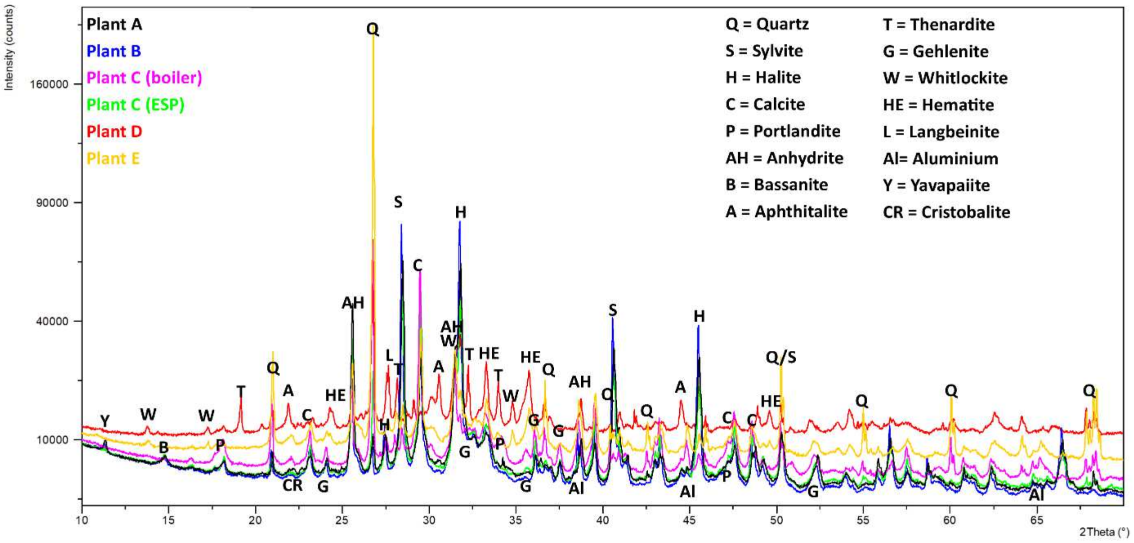

Figure 9. Powder XRD graphs (Cu Kα) of the six samples from MSWs. The visible difference in the background height is caused by the sample fluorescence (Fe) and possible differences in the amorphous content [23].

In Figure 10, the diffractogram of a fly ash sample from the paper and pulp industry has been illustrated. XRD shows high content of free lime (CaO), as confirmed by the XRF results. Calcite ($CaCO_3$), silicon oxide (SiO_2), calcium silicate in the form of Ca_2 (SiO_4), and aluminum silicate in form of mayenite ($Ca_{12}Al_{14}O_{33}$) and gehlenite ($Ca_2Al_2SiO_7$) are the other mineral compounds detected in this type of fly ash.

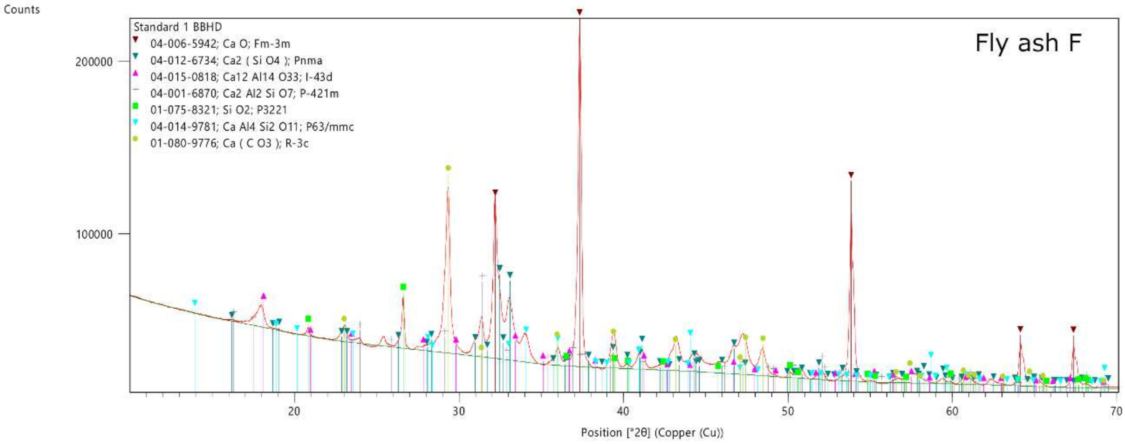

Figure 10. Powder XRD graphs (Cu Kα) of fly ash F from the paper and pulp industry.

Figure 11 shows the result of X-ray analysis of a sample from a biomass plant. It shows a complex phase composition. It contains a large amount of quartz and calcite. Silicates appeared in the form of feldspar, belite, and gehlenite. This sample contains alkalis in the form of sulfates such as anhydrite ($CaSO_4$), arcanite (K_2SO_4), thendarite (Na_2SO_4), and glauberite ($CaNa_2(SO_4)_2$) as well as chlorides, halit (NaCl), and sylvite (KCl).

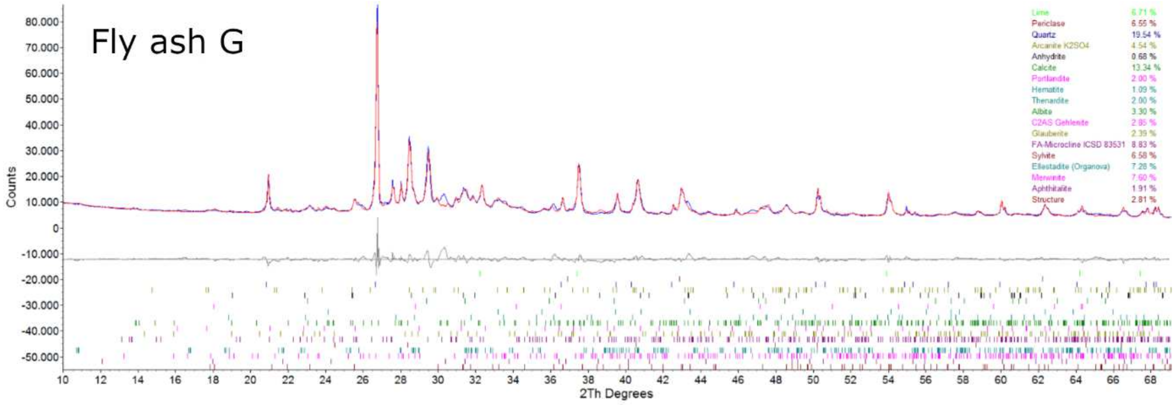

Figure 11. Powder XRD graphs (Cu Kα) of fly ash G from the biomass industry [39].

4.2.3 Simultaneous Thermal Analysis (STA)

To evaluate the usage of byproduct or waste as thermochemical and CO_2 storage material, thermogravimetric analysis (TGA) was performed. For any material to be considered as TCES, the material should fulfill some requirements. The following requirements are the minimum criteria [40]:

1. Reversible endothermic reaction through thermal treatment (charging).
   $A_{(s)} \leftrightarrows B_{(s)} + C_{(g)}$
2. Reversible exothermic reaction with gaseous components (discharging).
   $B_{(s)} + C_{(g)} \leftrightarrows A_{(s)}$
3. Cycling stability test (multiply heat storage/charging and heat release/discharging).

After fulfilling the above requirements, other criteria such as availability, price, and toxicity of the material should be considered [41]. Because of the easy separation of solid and gas components of the products ($B_{(s)}$, $C_{(g)}$), gas-solid reactions are preferable.

The endothermic reactions of most fly ash samples were detected using differential scanning calorimetry (DSC) signals followed by thermal decomposition (loss of mass/TG signal). Figure 12 shows a result of TG and DSC runs of an MSW fly ash sample up to 1150 °C under a nitrogen atmosphere. Three steps of mass loss can be identified at different temperature ranges. A mass loss of 1.8% occurs because of loss of moisture and volatilization of organic components up to 500 °C. The second mass loss of 4.1% occurred in the temperature range between 500 and 754 °C because of dehydration of metal hydroxides such as calcium hydroxide and other existing metal hydroxides in the fly ash sample, and the third and last mass loss of 26.6% occurred from the decomposition of carbonates, sulfates, and metals salts [42,43].

Depending on the origin of the fly ash sample, the chemical composition and combustion technologies (grate furnace, fluidized bed, and rotary kiln) used for the combustion distinguish the trend of mass loss of TGA. In general, two, three, or even four steps of mass loss can be identified by a thermal treatment of fly ash sample from different industrial sectors on TGA signal. The energy contents of fly ash samples can be calculated by integration and addition of endothermic peaks generated on the DSC signal.

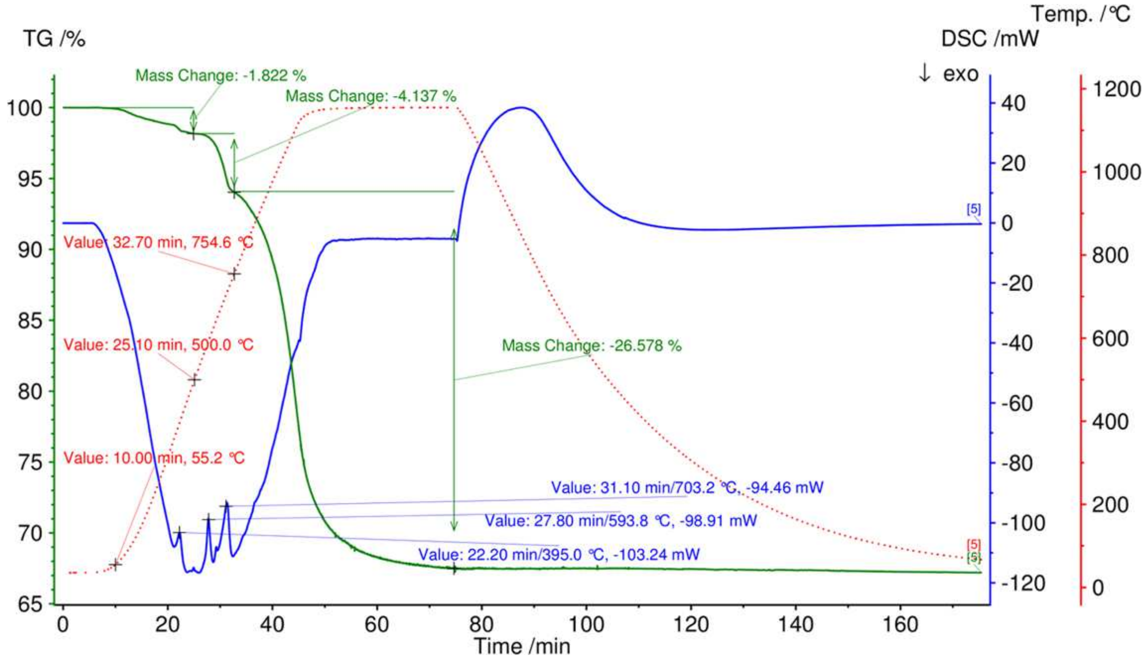

Figure 12. Thermal decomposition of fly ash sample B under an N_2 atmosphere. The green, blue, and dotted red lines show the percentage of mass loss based on TG, DSC, and the temperature profile, respectively [38].

Table 5 represents the results of the energy contents of fly ash sample by thermal treatment up to 1150 °C from different industrial sectors. The energy content of the fly ash sample generated from the paper and pulp industry was the highest followed by the fly ash C-boiler from MSW and fly ash G from biomass.

The energy content of the fly ash sample generated by grate furnace technology was about 92 kJ/kg in average, expect of fly ash C-boiler with 394 kJ/kg, the highest energy content among all fly ash sample from MSWIs. Fly ash E from fluidized bed technology of municipal solid waste showed an energy of 50 kJ/kg, and no endothermic peak was detected for fly ash D from rotary kiln. The energy content of fly ash F from fluidized bed technology showed with 650 kJ/kg the highest energy content among all fly ash samples and fly ash G from fluidized bed from biomass indicated an energy content of 250 kJ/kg.

Table 5. Energy Content in kJ/kg of fly ash samples.

Fly ash	A	B	C-boiler	C-filter	D	E	F	G
Energy content	94	85	394	98	n.d.	50	650	250

The second requirement, which is the exothermic reaction of charged form of fly ash with gaseous compounds (CO_2/H_2O), was tested for the fly ash samples. The results revealed that fly ash C-boiler and fly ash sample F were able to react with mixture of CO_2 and H_2O atmosphere. Figure 13 illustrates the charging step of fly ash C-boiler sample under a nitrogen atmosphere up to 880 °C followed by exothermic reactions detected using DSC signals. The exothermic reaction of discharging was identified using DSC signals of the charged form of fly ash sample under a CO_2 atmosphere and 0.2 bar water vapor pressure by cooling the system to the ambient temperature. The stored heat up to 880 °C was about 240 kJ/kg, one third of which could be released under CO_2 and water vapor atmosphere.

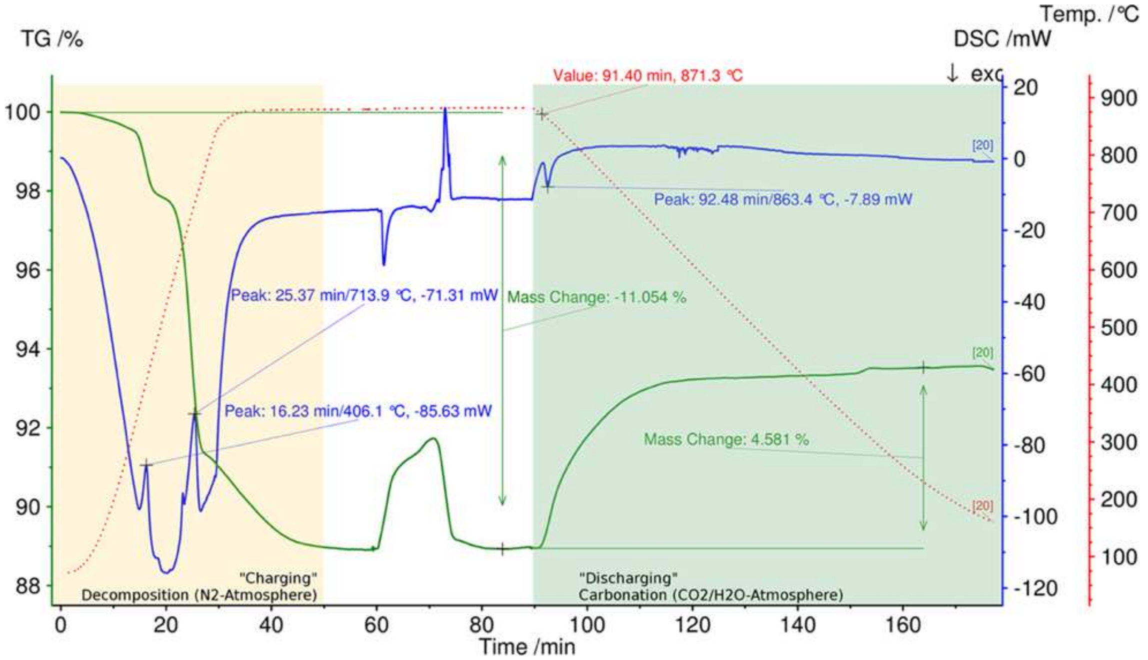

Figure 13. Decomposition of fly ash C-boiler sample under inert N_2 atmosphere at 880 °C and the switch to a CO_2/H_2O atmosphere. The green, blue, and dotted red lines show the percentage of mass loss based on TG, DSC, and the temperature profile, respectively [38].

Figure 14 demonstrates the results for the fly ash sample F from the paper and pulp industry. Despite to fly ash C-boiler sample the reserves reaction showed a significant mass increase of 13.6% more than mass loss of 10% (charging step), owing to intermediate state of this kind of sample and chemical component in particular CaO and $Ca(OH)_2$, which have not been totally carbonated.

Endothermic and exothermic peaks of the DSC signals became larger and clearer compared to those of the fly ash C-boiler sample. The stored heat energy up to 880 °C was about 300 kJ/kg (charging), and the release of heat energy was about 490 kJ/kg (discharging).

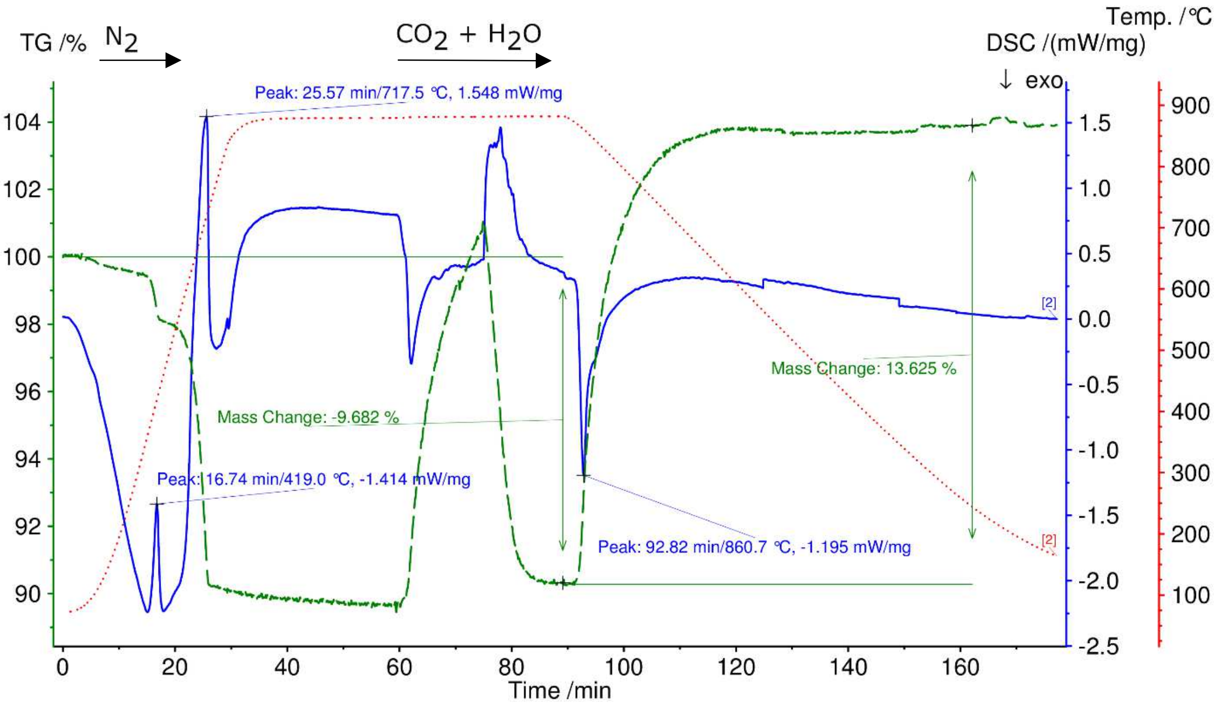

Figure 14. Decomposition of fly ash sample F under inert N_2 atmosphere at 880 °C and the switch to a CO_2/H_2O atmosphere. The green, blue, and dotted red lines show the percentage of mass loss based on TG, DSC, and the temperature profile, respectively.

The third requirement, cycling stability test, was performed for the fly ash C-boiler sample. The experimental condition was the same as that of the previous experiment, but the temperature was maintained at 350 °C for carbonation. Three cycles of heat storage and release were accomplished using this fly ash sample. Figure 15 represents the cycling stability test. The first mass loss of 15% occurred because of the decomposition of sulfates and carbonates and evaporation of heavy metals or their chloride forms with lower boiling points such as Zn and Cd. Therefore, this mass loss was more compared with the mass loss in the next steps. Except the first mass loss, the mass increase (charging step) and mass decrease (discharging step) were stable, and the time of carbonation (mass increase) was less than 40 minutes.

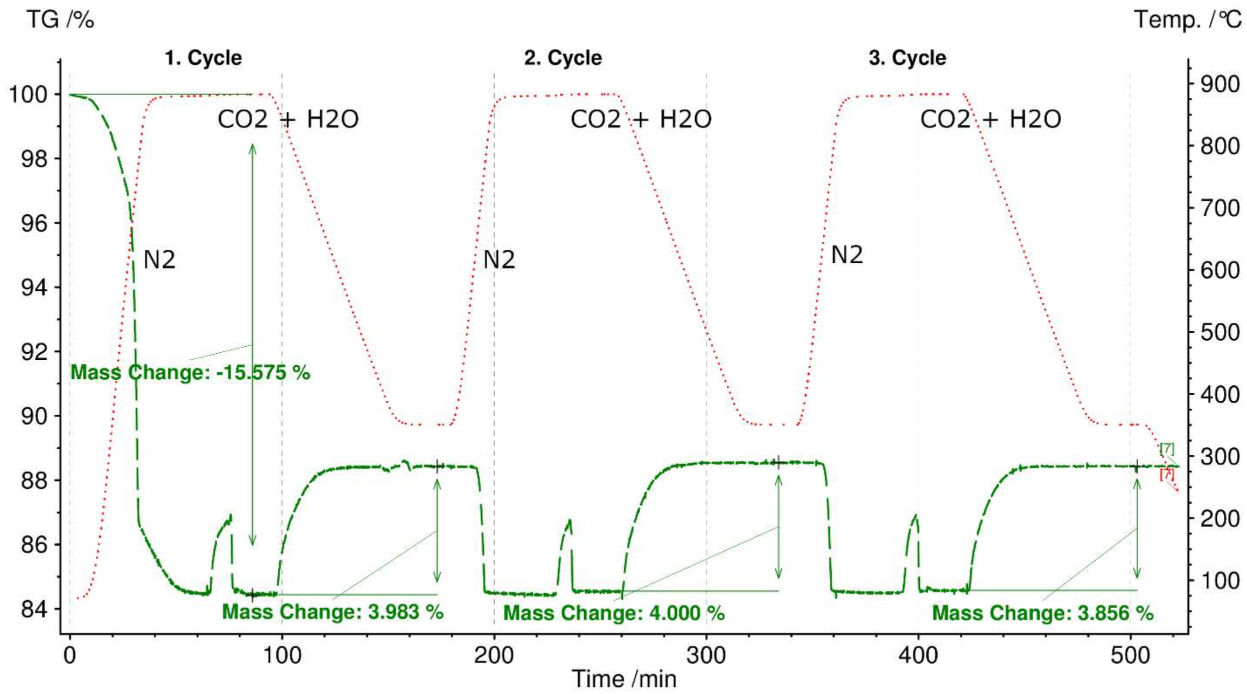

Figure 15. Cycling stability test of fly ash C-boiler heated to 880 °C at a heating rate of 30 °C/min in a N_2 atmosphere (charging step) and cooled from 880 °C to 350 °C at a cooling rate of 10 °C/min in CO_2 (100 ml/min) and H_2O (1 g/h) atmosphere [23].

Figure 16 shows the result of the cycling stability test for fly ash F, which indicates the ability of this type of fly ash to store and release heat for a minimum of three times. However, a slight alteration of materials can be seen in the second and third cycles (charging and discharging) because of not reaching the full conversions compared with the first cycle.

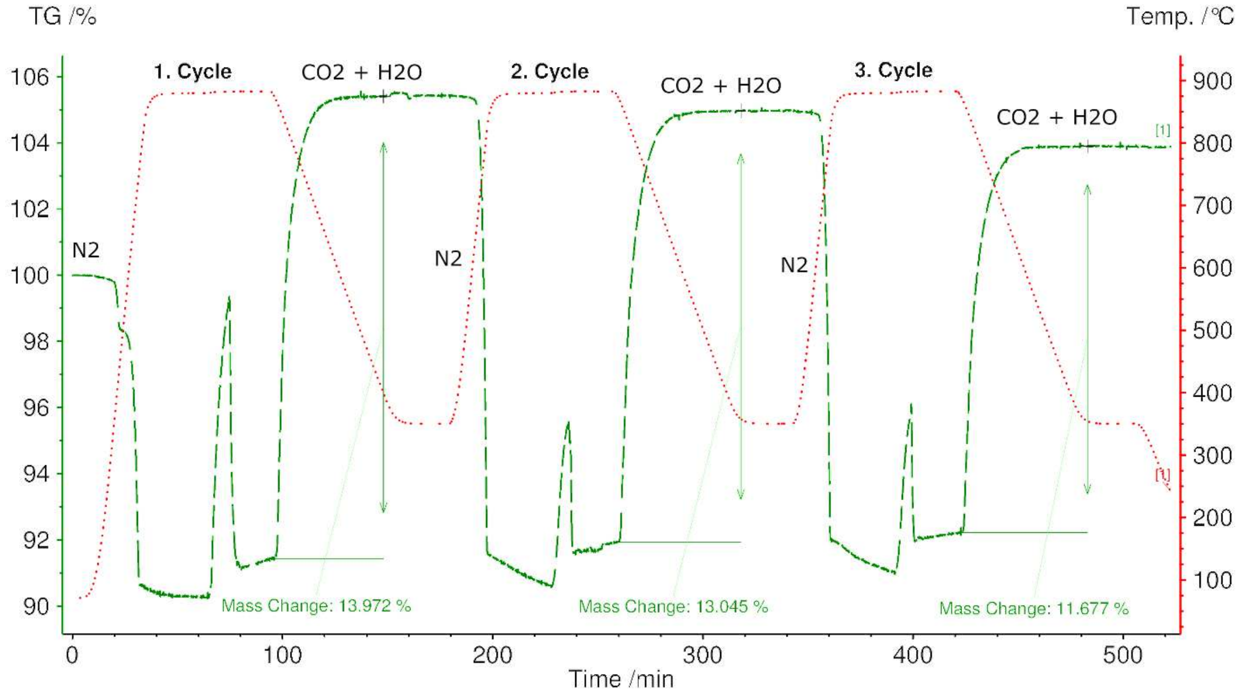

Figure 16. Cycling stability test of fly ash F heated to 880 °C at a heating rate of 30 °C/min in a N_2 atmosphere (charging step) and cooling from 880 °C to 350 °C at a cooling rate of 10 °C/min in CO_2 (100 ml/min) and H_2O (1 g/h) atmosphere.

Table 6 exhibits the amount of heat stored and release in each charging and discharging step, respectively.

Table 6. Specific energy content of charging and discharging steps of fly ash C-boiler (in kJ/kg) [23].

Energy content in kJ/kg	1. Cycle	2. Cycle	3. Cycle
Charging (heating to 880 °C, N_2 atmosphere)	290	99	105
Discharging (cooling from 880 °C to 350 °C, CO_2 and H_2O atmosphere)	73	101	100
Charging fly ash F (heating to 880 °C, N_2 atmosphere)	298	403	393
Discharging fly ash F (paper and Pulp) cooling from 880 °C to 350 °C, CO_2 and H_2O atmosphere)	504	470	421

The reactivity of the fly ash samples was tested under different atmospheres (N_2, air, H_2O, and CO_2). In paper III, the results are presented and discussed. Figure 17 shows the thermogravimetric analysis of fly ash C-boiler under a pure CO_2 atmosphere by thermal treatment up to 1150 °C. The mass signal increased by about 2.7% followed by an exothermic reaction detected on DSC signals, which was because of the reaction of this fly ash sample with CO_2 up to 710 °C. By increasing the temperature beyond 710 °C, the mass signals started to decrease because of endothermic decarbonation

(DSC signal). This type of fly ash shows a CO_2 storage capacity of 27 kg CO_2/ton under this experimental run.

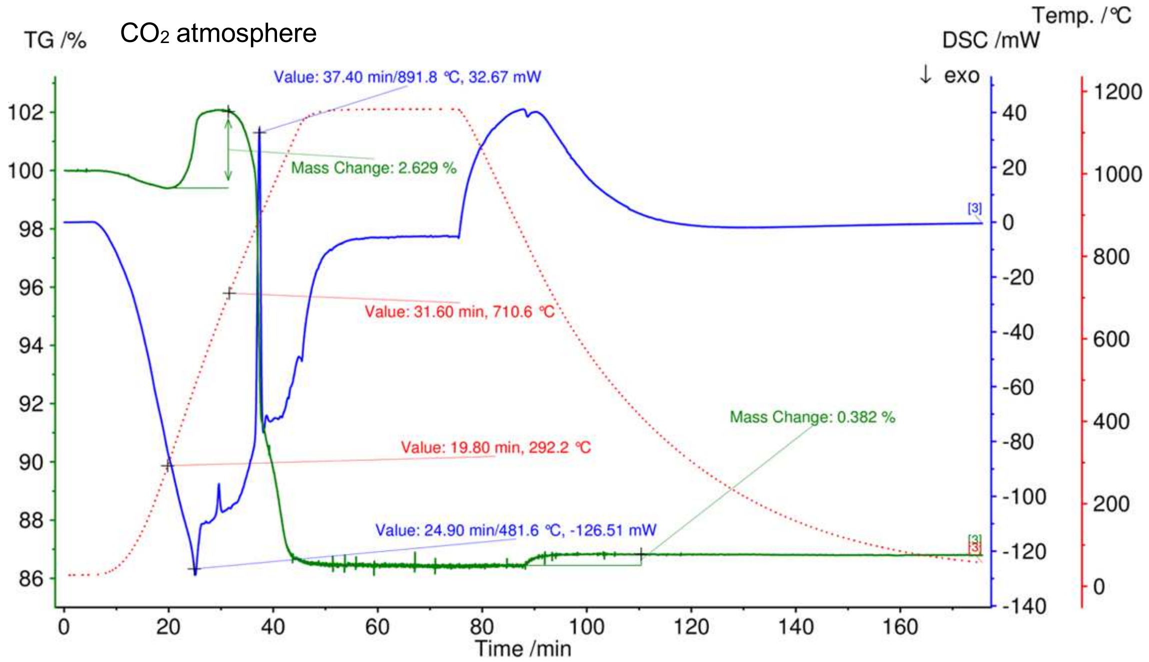

Figure 17. Thermal behavior of fly ash sample C under CO_2 atmosphere up to 900 °C. The green, blue, and dotted red lines show the percentage of mass loss based on TG, DSC, and the temperature profile, respectively [38].

The reactivity of other fly ash samples under pure CO_2 atmosphere and their comparison with fly ash C-boiler are shown in Figure 18. Among the MSW fly ash samples, only the fly ash C-boiler sample could store CO_2.

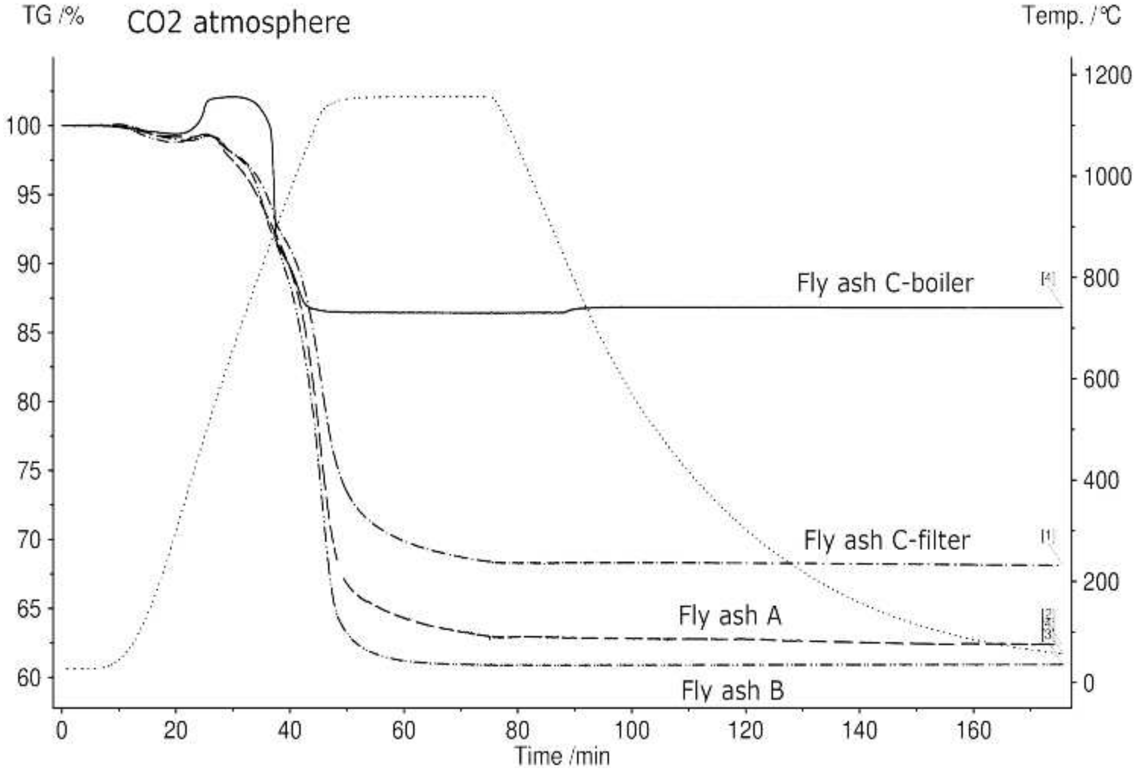

Figure 18. Comparison of thermogravimetric (TG) curves of fly ash samples from MSWIs under CO_2 atmosphere [23].

Fly ash G from biomass was found to be reactive under a CO_2 atmosphere similar to the fly ash C-boiler sample from MSW. Figure 19 illustrates the reactivity of this fly ash. The mass increase of 1.7% (w/w) was observed by thermal treatment up to 661 °C, which means a CO_2 storage capacity of 17 kg/ ton fly ash. Whereas, the fly ash C-boiler, the mass signal (green line) showed up two steps to reach 1.7% (w/w). The first mass increase of 1% was observed from 302 °C to 506 °C and the second of 0.7% from 506 °C to 661 °C.

Figure 20 represents the high reactivity of fly ash F from the paper and pulp industry with CO_2. A mass increase of 11.2% in two steps is visible. The first step of about 5% occurred from 323 °C to 502 °C, and the second mass increase of 6.2% occurred from 502 °C to 833 °C.

The first step may have occurred because of the reaction of CO_2 with the surface of particles, whilst, the second step may be an indication of reaction front inside the particles.

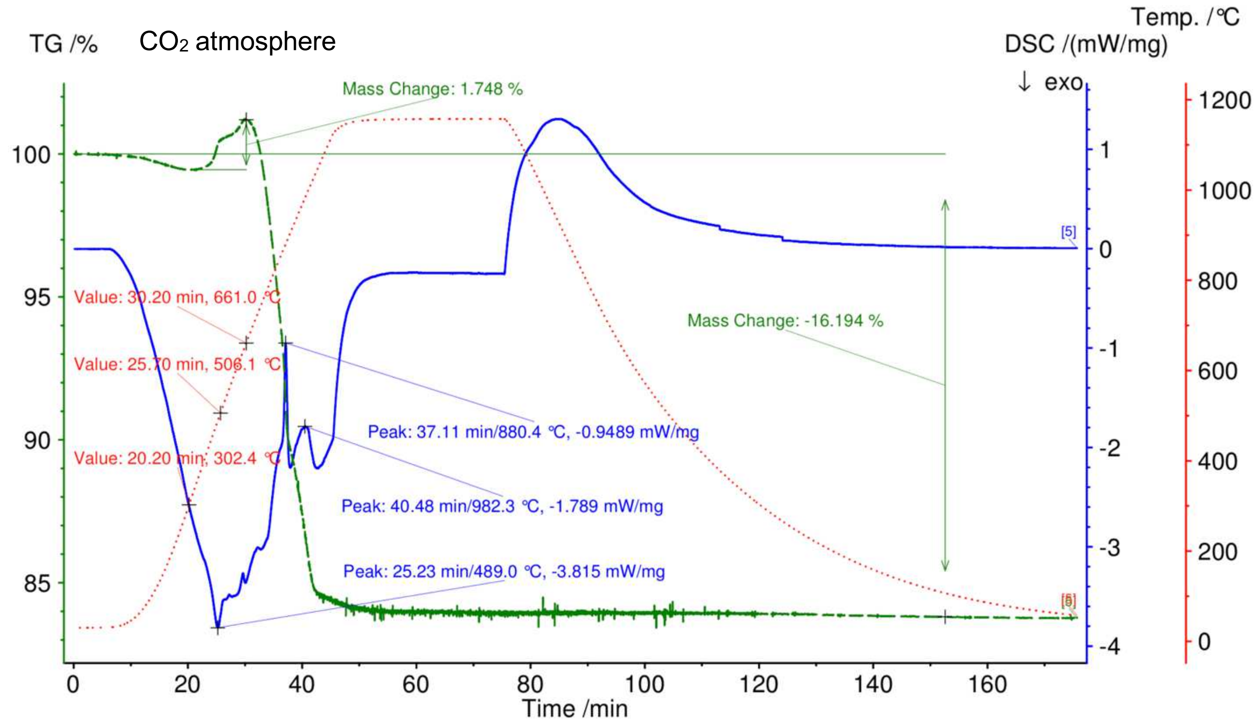

Figure 19. Thermal behavior of fly ash G sample under CO_2 atmosphere. Thermogravimetric (TG) curves are represented as the green line and the differential scanning calorimetry (DSC) results is in blue. The dotted red line indicates the temperature profile.

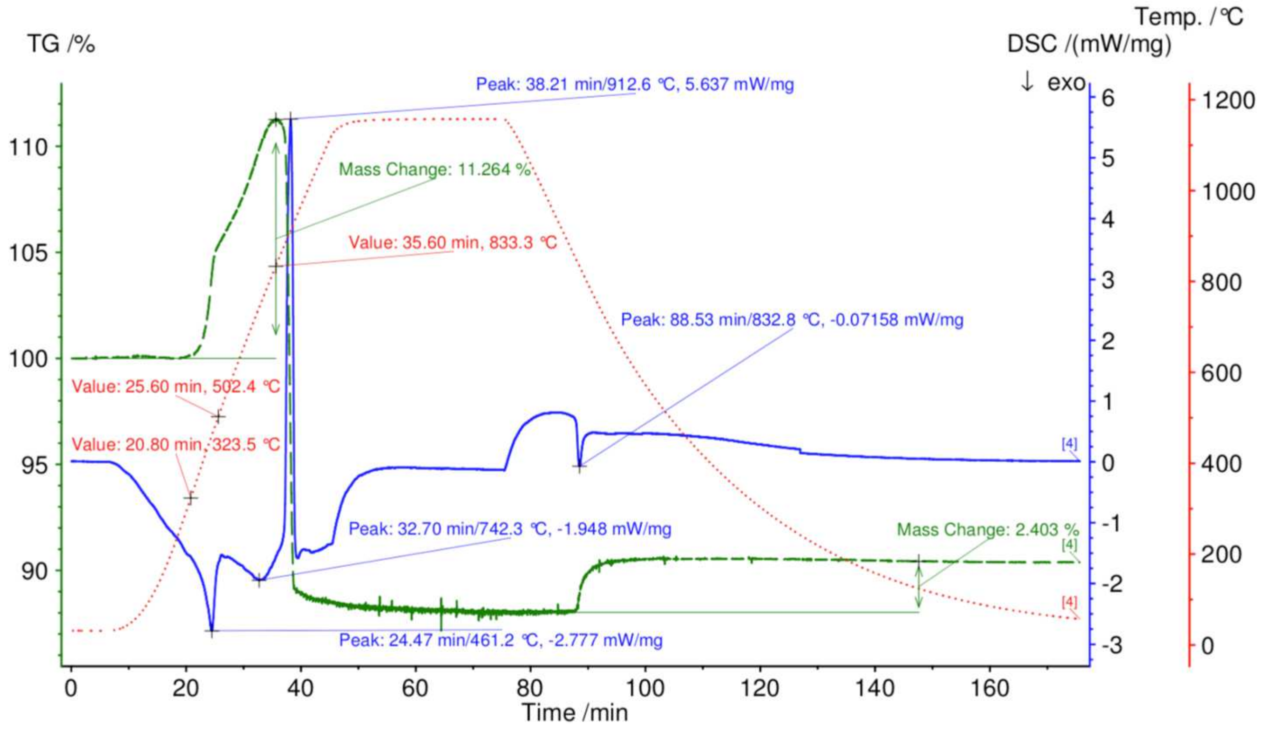

Figure 20. Thermal behavior of fly ash F sample under CO_2 atmosphere. The thermogravimetric (TG) curve is in green and the differential scanning calorimetry (DSC) curves is in blue. The dotted red line indicates the temperature profile.

4.2.4 Leaching Test

Table 7. Leaching contents (mg/kg) of heavy metals from ash samples [23].

Element Components	Limits value	A	B	C-boiler	C-filter	D	E
Al		1.9	2.1	1.61	1.51	3	1471
Sb	0.7 (2.1)	0.05	0.07	0.05	0.06	0.21	0.2
As	2	0.116	0.07	0.05	0.13	-	0.05
Ba	100 (300)	5.61	4.7	4.8	5.75	1.5	74
Pb	10 (30)	294	304	16.7	52.55	24	2.03
Cd	1	0.12	0.21	0.18	0.18	144	0.1
Cr	10 (20)	2.3	2.6	6.5	7.8	1.1	0.9
Co	5	0.1	0.17	0.18	0.18	2.7	0.1
Fe		0.15	0.4	0.55	0.24	0.7	0.12
Cu	50	0.1	0.21	0.166	0.2	1.3	0.18
Mn		0.1	0.17	0.166	0.18	27	0.1
Ni	10	8.9	5.8	4.8	1.7	7.2	1.3
Hg	0.1	0.11	0.18	0.183	0.22	0.01	0.1
Ag	1	0.01	0.01	0.01	0.01	0.6	0.01
Zn	50 (100)	0.07	0.05	0.05	0.05	2.1	0.05
Sn	20	0.1	0.15	0.18	0.18	0.4	0.1
NH_4	300	0.1	0.17	0.18	0.18	2.2	0.1
Cr(VI)		9.1	5.6	5.05	2.7	0.5	
F	150	1.7	0.6	5.05	5.5	162	0.08
NO_2–N	15	1	1	1	1	1	1
PO_4	50	37.5	43.7	18.3	33.48	2.7	5.26
SO_4		1	1	1	1	147	1
PH		11.9	11.8	11.1	12.3	8.8	11.28
Electrical conductivity (mS/cm)		40.5	43.35	37.43	16.71	31	67

To evaluate the environmental impact of fly ash samples, a leachability test was performed according to the norm (EN 12457-4). The results of this test are illustrated in Table 7. The electrical conductivities and pH values are also presented in the same table as simultaneously measured parameters according to the aforementioned norm. The lower limit values and the highest limit values (in brackets) for non-hazardous-waste according to the Austrian Landfill Ordinance are included in a separate column.

The element Pb in all fly ash samples, expect fly ash C-boiler and E (fluidized bed) samples, was above the highest limit value for non-hazardous-waste. In case of fly ash A and B, the Pb contents are around 10 times higher than the highest limit value of 30 mg/kg. The Pb content of the fly ash C-boiler sample is 16.7 mg/kg.

Cd from fly ash D from the rotary kiln (hazardous waste) was 144 mg/kg, which is significantly higher than the set limit value of 1 mg/kg.

The leached content of element Mn (27 mg/kg) is higher than that of other fly ash samples. The Hg content of fly ash C-filter with a value of 0.2 mg/kg is slightly higher than the limit value of 0.1 mg/kg for non-hazardous-waste. The leached contents of other elements are all below the set limit value by the Austrian Landfill Ordinance.

The thermal treatment of the fly ash sample can positively affect the leaching behavior of metals because of a reduction in the porosity through sintering and agglomeration of particles. To evaluate this positive effect on leaching behavior of elements, further investigation was carried out in a muffle oven at the same heating rate and temperature as that set in STA runs for fly samples A and B to obtain the required amount for leachate analysis. The fly ash samples were heated up to 900 °C at a heating rate of 30 °C/min and maintained at 900 °C for 30 minutes under an ambient atmosphere. The leaching content elements of thermally treated samples was significantly improved except for Cr element for the performed fly ash samples (Table 8).

Table 8. Leaching contents (mg/kg) of heavy metals from ash samples A and B after thermal treatment up to 900 °C for 30 minutes.

Elements/components	Limit value	Fly ash A untreated	Fly ash A treated	Fly ash B untreated	Fly ash B treated
Al		2.07	0.11	1.51	0.61
Sb	0.7 (2.1)	0.07	< 0.002	0.06	< 0.002
As	2	0.07	< 0.003	0.13	< 0.003
Ba	100 (300)	4.72	0.14	5.75	0.16
Pb	10 (30)	304.75	< 0.0036	52.55	< 0.0036
Cd	1	0.21	< 0.001	0.18	< 0.001
Cr	10 (20)	2.63	23.6	7.88	9.6
Co	5	0.17	< 0.009	0.18	< 0.009
Fe		0.41	< 0.005	0.24	< 0.005
Cu	50	0.21	< 0.003	0.2	< 0.003
Mn		0.17	--	0.18	--
Ni	10	5.87	< 0.003	1.78	0.004
Hg	0.1	0.18	0.002	0.22	0.001
Ag	1	0.01	--	0.01	--
Zn	50 (100)	0.05	< 0.003	0.053	0.006
Sn	20	0.15	< 0.015	0.18	< 0.015

Carbonation also has a positive effect on the leachate of heavy metals in fly ash samples, in addition to positive thermal treatment. However, these effects of thermal treatment and carbonation need to be studied further.

4.2.5 SEM Analysis

The results of SEM analysis performed for all types of fly ash samples before (as received) and after thermal treatment up to 1150 °C under N_2 atmosphere in the STA revealed sintering and agglomeration of particles. Some fly ash samples were melted (E and D). Thermal treatment up to 1150 °C for decomposition (charging step) can negatively impact the cycling stability test which is an essential requirement for TCES. However, all fly ash samples except fly ash sample E (fluidized bed) and sample D (rotary kiln) were easily removable from STA crucibles, although they were in a compacted powder form. Figure 21 shows the SEM analysis results of fly sample A.

To reduce the sintering and agglomeration effect and to be close to the applicable temperature for the combustion process, a temperature of 880 °C was used for the decomposition of the fly ash samples (charging step), and a cycling stability test for the fly ash C-boiler sample was performed. As already shown in Figure 15, the sintering and temperature did not negatively affect the carbonation and decarbonation of the selected fly ash sample for three cycles.

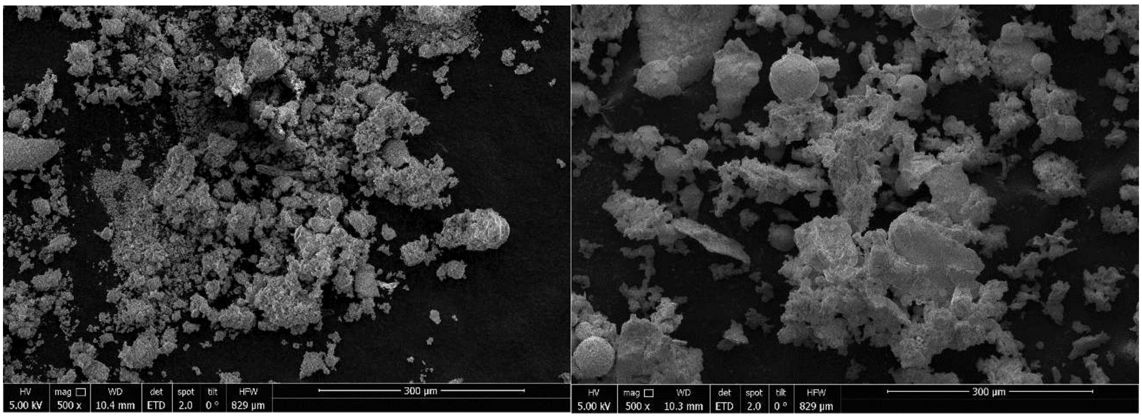

Figure 21. SEM analysis of fly ash samples before (left) and after (right) STA experiments [38].

4.2.6 System Integration

System integration for the application of suitable fly ash samples/fractions as TCES and CO_2 storage material is the key for the implementation on the industrial scale. In general, two methods for the mineral carbonation process exist—in situ and ex situ carbonation. Ex situ mineral carbonation is divided into direct and indirect mineral carbonation, which can also be performed as a dry or wet process [44]. Direct mineral carbonation is the simplest approach because of direct gas-solid carbonation [44], and the wet process is preferable because of the acceleration of carbonation kinetics in the presence of moisture in the gas or aqueous form [22].

“In Figure 22, on the left side, some different waste and biomass combustion technologies are presented, which can deliver fly ash for CO_2 storage purposes. The fine fly ash particles can be separated from the flue-gas stream at the heat exchanger as boiler ash or at particle separators as cyclones or filters. The fly ash is stored in appropriate storage facilities according to the intended storage duration (short time or seasonal storage).

Charging (excess heat utilization) and discharging/CO_2 binding (heat release) of fly ash can be accomplished as an external process (using separate reactors) or by applying an in-situ approach for discharging, and CO_2 fixation can be done by adding the charged (decarbonated) fly ash to the heat exchanger part of the plant and exposing it to CO_2 in the flue gas; charging is carried out by feeding the discharged (carbonated) fly ash into the burning chamber. As an alternative, discharging can also be done in a slurry reactor (at the same time as ash stabilization). It is also possible to utilize the energy storage material off-site by transporting it to remote energy extraction facilities by truck, train, or pipelines to make use of the stored thermal energy. Aged or excess fly ash can be used in cement industries and construction sites or as a stabilization material (binder) in landfill operations. Stabilized fly ash could also be landfilled directly.” [23]

Table 9 simplifies the pathways described in figure 22.

Table 9. Pathways for fly ash application as TCES and CO_2 storage

In-situ (in the same combustion)	Ex-situ (in separate reactors)
➢ High temperature region ○ Calcination (charging, heat consumption), heat from in situ process	➢ Charging from any waste heat
➢ Low temperature region ○ Carbonation/CO_2 storage (discharging, heat release), handling of flue gas	➢ Discharging, heat release, carbonation (dry/wet), for heating and stabilization, CO_2 storage

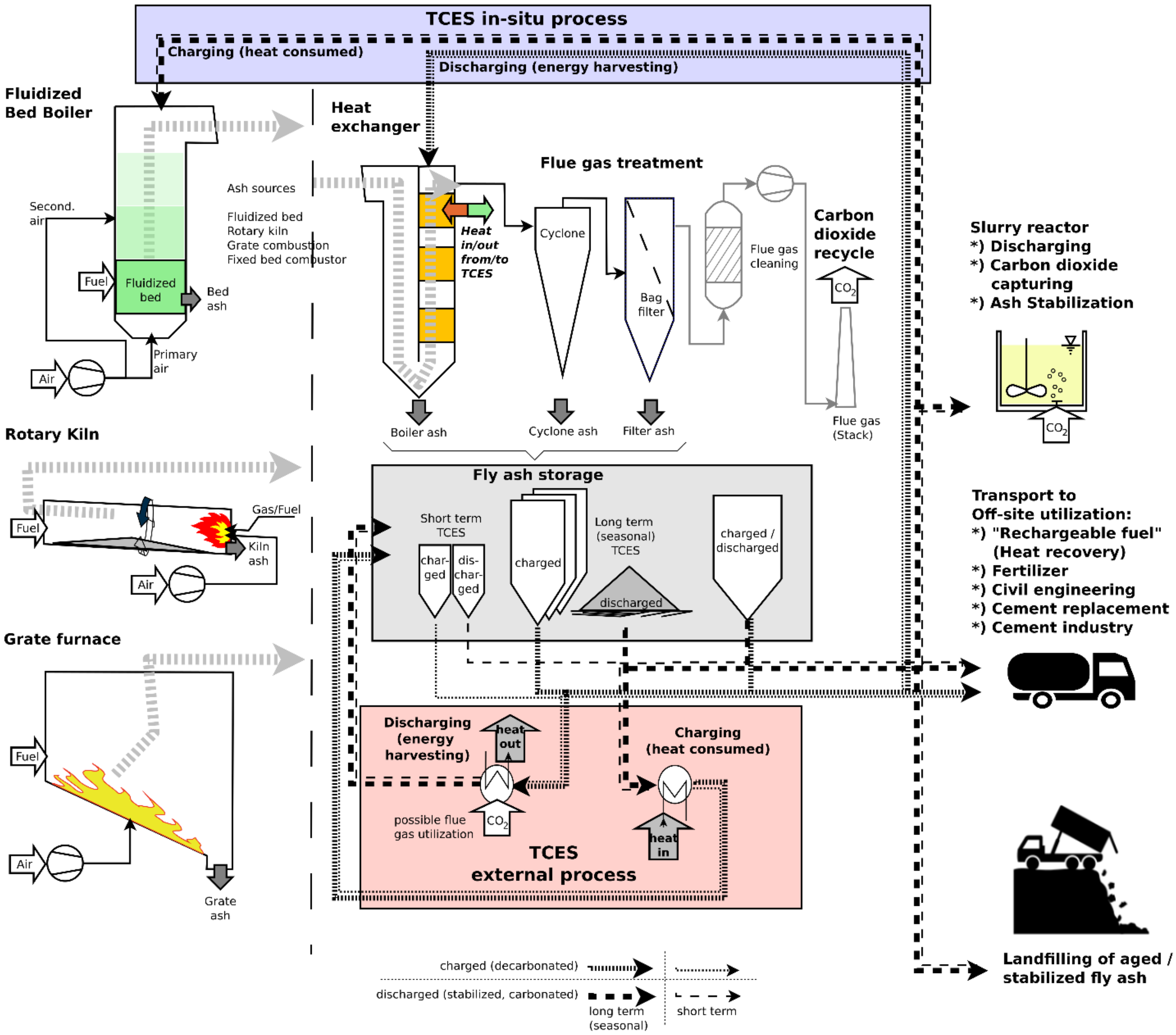

Figure 22. Schematic overview of the process combination related to the utilization of fly ash as TCES or CO_2 capture materials [23].

5 Scientific Contribution of the Thesis

In the big picture, the aim of this work was to contribute to sustainable energy sources. Particularly, materials that can store surplus energy from solar power plants or waste heat from any plant for further use and for seasonal storage. The storage of energy from sustainable energy sources such as sun is essential to increase the efficiency of those plants and to make them competitive as fossil-fuel energy sources. The CuO/Cu_2O system is a suitable TCES material for storage of heat energy at high temperatures, which can be used in CSP. However, for application as TCES, the kinetics of this system have not gained enough attention. Therefore, kinetic evaluation was done to determine the kinetics (activation energy, model, and frequency factor). In addition, the impact of partial pressure on the oxidation kinetics was identified.

More importantly, the focus of material search for TCES has relied on pure or doped materials. The use of pure or doped materials involves a high cost and has a negative environmental impact, which, from the economical and sustainable point of view, is challenging for industrial implementation of TCES technology in future, in contrast with all benefits that this technology possesses.

The main contribution of this thesis is to expand the search for optimal TCES materials and to consider byproducts or waste from industries. As long as TCES is under development, it makes more sense to expand our views and to investigate the potential of waste and byproducts from industries for their use as TCES material. The target and final destination of any technology is its industrial application. Essential issues are the cost and advantages which any new technologies provide. The reuse of byproducts and waste is a common interest of industries and researchers, and the social awareness of humans for environmental protection may lead to faster development of TCES.

An important scientific contribution of this thesis is the investigation of CO_2 capture and storage through carbonation reaction of fly ash with CO_2. Therefore, the storage capacities of fly ash from different industrial sectors are evaluated. In addition, the energy gain from the exothermic carbonation reactions under different temperature and atmosphere are evaluated from the results of STA.

6 Conclusions and Outlook

Climate change is a global problem that needs global action of humans worldwide. To overcome this challenge, industries need to adopt processes to reduce CO_2 emissions. Researchers need to make contributions by supporting industries to provide them with the tools or ideas which can be beneficial for controlling and mitigating global CO_2 emissions.

TCES is a modern technology and one reasonable option that can contribute to make the renewable energy sources more sustainable by storing surplus energy for the time when it is needed. Among all material for usage in concentrated solar power (CSP) plants, CuO/Cu_2O with an energy content of 810 kJ/kg is an interesting option. However, the knowledge of kinetics of any system is essential for designing a system. In the frame work of this thesis, the kinetics (model, activation energy, and frequency factor) and the effect of partial pressure on the oxidation reaction of Cu_2O to CuO are investigated using the extended NPK method. The best fitted model is the nucleation model of Avrami und Erofeev (A2). The activation energies were 236 kJ/mol and 233 kJ/mol depending on whether the stoichiometry factor is considered in the partial pressure term or not, respectively. Reparameterization of the pressure term from P to $1-(P/P^*)^n$ is necessary to consider the distance of equilibrium in the general kinetic equation.

In addition, this thesis tries to bring awareness for researchers in the field of TCES to focus from pure or doped materials and to byproducts and waste from industries. Some fly ash samples from MSW (fly ash C-boiler) and paper and pulp industries (fly ash F) could fulfill the minimum requirements (charging, discharging, and cycling stability test) to be considered as TCES materials. Therefore, fly ash samples F, C-boiler and G with the energy contents of 650, 394 and 250 kJ/kg respectively, are promising for further investigation as TCES and CO_2 storage material.

Furthermore, mineral carbonation of fly ash samples is another advantage of simultaneous harvesting of energy. Carbonation of fly ash can also lead to a better and stable product in case of fly ash from pulp and paper industries for further use or to generate a waste with less porosity through carbonation, which could be landfilled with less amount of cement added for stabilizing process. According to the STA results, there are some fly ash samples that can store CO_2 with a storage capacity in the range of 27 kg/ton to 130 kg/ton fly ash, based on the received form. However, further studies are needed to investigate the effect of carbonation on each fly ash sample with different mineral carbonation routes, owing to the difference in chemical composition of fly ash from industry to industry.

Storing excess heat in chemical form in fly ash or CO_2 capture by fly ash and generating a stabilized product for further use or landfilling are issues presented in this thesis which will contribute to protect the environment.

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8 Appendix (Papers I-III)