

Article



Particle Size Distribution and Enrichment of Alkali and Heavy Metals in Fly Ash on Air and Oxy-Fuel Conditions from Sludge Combustion

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Abstract: Comparative tests in air and oxy-fuel combustion were conducted in a 30 kW_{th} circulating fluidized bed (CFB) pilot plant for waste sludge combustion. General combustion characteristics of the CFB, such as pressure profiles, temperatures along the bed, and flue gas composition, were different under the air and oxy-fuel conditions. At the bottom and in the fly ash, alkali and heavy metals had different distributions under the air and oxy-fuel combustion conditions. The particle size distribution in fly ash from air combustion was dominated by coarse particles, over 2.5 μ m in size, whereas with oxy-fuel combustion, most particles were submicron in size, approximately 0.1 μ m, and a smaller quantity of coarse particles, over 2.5 μ m in size, were found in the ashes from oxy-fuel combustion and in higher quantity than those found in air combustion. Submicron particle formation from Cr, Ni, Cu, and Zn in the fly ash occurred more during oxy-fuel combustion than it did in air combustion.

Keywords: waste sewage sludge; oxy-fuel combustion; circulating fluidized bed; particle size distribution; alkali and heavy metals

1. Introduction

Recently, the need for waste to be converted to energy has emerged globally. Waste sewage sludge is one of the renewable energy resources, and the amount of it has gradually increased over the years in Korea, where it reached up to 20 million tons in 2020. Since ocean dumping was prohibited after the international prohibition of waste sludge was announced in 2012, technology to convert waste sludge to energy has developed as an alternative disposal option.

The capacity of commercial fluidized bed combustion (FBC) plants for waste sludge is between 50 and 300 tons per day. These commercial plants combust waste sludge by utilizing air, generating much carbon dioxide, which is a greenhouse gas (GHG).

However, GHGs have become a worldwide issue, and converting waste, such as sludge, biomass, and municipal solid waste, to energy has been identified as a secondary source of GHG emissions, with fossil fuel combustion deemed a primary emission source. To mitigate global warming, carbon capture and storage (CCS) technology was developed to reduce GHGs, such as carbon dioxide, from anthropogenic emission sources. The effects of GHGs on global warming are acknowledged worldwide; therefore, GHG emission reduction has increased in importance.

Oxy-fuel combustion consumes a combination of oxygen greater than 95% in purity and recycles flue gas, which is enriched with carbon dioxide. During oxy-fuel combustion, a gas consisting primarily of carbon dioxide is generated that is ready for sequestration without stripping of the carbon dioxide from the flue gas. Due to the different surroundings



Citation: Jang, H.-N.; Yoo, H.-M.; Choi, H.S. Particle Size Distribution and Enrichment of Alkali and Heavy Metals in Fly Ash on Air and Oxy-Fuel Conditions from Sludge Combustion. *Energies* **2023**, *16*, 145. https://doi.org/10.3390/en16010145

Academic Editors: Tomasz Czakiert and Monika Kosowska-Golachowska

Received: 7 October 2022 Revised: 14 November 2022 Accepted: 26 November 2022 Published: 23 December 2022



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during combustion, the flue gas composition of oxy-fuel combustion should be different than it is with air combustion [1].

In waste sludge combustion, the flue gas includes various air pollutants, such as ash, heavy metals, sulfur oxide, and nitrogen oxide. Among these air pollutants, the behaviors of ash and heavy metals are especially important because these compounds incur adverse health effects and prevent economical operation by causing fouling of, and deposition on, the boiler tube. There are numerous studies about the behavior of ash and heavy metals during conventional waste sludge combustion [1,2]. Rink et al. [3] studied the behavior of ash during sewage sludge combustion using a 300 kW bubbling fluidized bed (BFB) combustor. According to this study, particle size distribution was different along the height of the BFB combustor. This might have occurred because of different particle formation mechanisms in each temperature region. In addition, particle shapes were different at each sampling location, which were related to the particle formation mechanism of heavy metals. Cenni et al. [4] investigated the recovery rate of heavy metals in bottom ash, cyclone ash, and filter ash by blending sewage sludge with coal using a 500 kW pulverized fuel combustion chamber. This study indicated that the recovery rate of metals tended to increase when the blending rate of sewage sludge increased due to a flame temperature difference, in comparison with coal combustion. Latva-Somppi et al. [5] studied ash deposition and size distribution from the combustion of sewage sludge with wood by comparing BFB and CFB combustors. According to this study, sewage sludge contained a high proportion of alkali metals, such as Al, Ca, Si, and K, which caused ash deposition in the refractory liners and boiler tube. It was found that ash deposition did not occur in the CFB combustor, due to the advantageous heat distribution of the CFB. In addition, ash size in the CFB was smaller than it was in the BFB because the time for particle growth from metals, which was the main cause of ash deposition, was shorter than it was for the BFB. Lopez et al. [6] investigated metal partitioning in bottom ash and fly ash in accordance with their volatility with variation in sludge mixture with coal using a 90 kW BFB pilot plant. According to the study, Hg, Cd, Cu, and Pb in the fly ash increased more significantly in the mixture of sludge with coal than in the coal alone, whereas Cr, Ni, Mn, and Zn in the fly ash were less significant. In addition, Hg, Cd, Pb, and Zn increased more in the fly ash than in the bottom ash, whereas Mn, Cu, Ni, and Cr were not as significant, which was likely related to the volatility of the metals. Marani et al. [7] studied the enrichment factor of metals, such as Cd, Cr, Mn, Ni, Pb, Ti, and Zn, in cyclone ash and fly ash from sewage sludge combustion by chlorine content using a 250 kg/h CFB pilot plant. According to the study, the concentrations of those metals were enriched more in the fly ash than they were in the cyclone ash. Regarding the enrichment factor, Cd and Cr increased as chlorine content increased, whereas other metals were not as significant, likely due to the difference in the volatility of metals and formation of metal chloride compounds. Amand and Leckner [8] studied mass balance of trace metals from co-combustion of sludge, with coal or wood as the base fuel, by using a 12 MW_{th} CFB boiler. The study indicated that the trace metals in ash increased when wood was the base fuel as the sludge mixing rate increased, whereas this trend was not present when coal was the base fuel. Regarding the mass balance of trace metals in ash, volatile matter, such as Hg and Cd, was enriched in the fly ash from a second cyclone and bag filter, but non-volatile matter, such as Mn, was evenly enriched in the bottom ash and fly ash during co-combustion of coal and sludge. However, non-volatile matter was enriched in the finest fly ash during co-combustion of wood and sludge. Elled et al. [9,10] studied relative enrichment of volatile matter and non-volatile matter at different sampling points, such as the bed ash, second cyclone ash, and bag-filter ash, from co-combustion of wood and sludge. The study indicated that as the sludge mixing rate increased, the enrichment rate of volatile matter increased more in the fly ash than it did for the non-volatile matter in the fly ash. As mentioned above, there has been numerous research works related to the behavior of ash and heavy metals during FBC incineration. In summary, the studies concluded that the fate of trace elements was influenced by fuel type, combustion facility type, and operating conditions (temperature, pressure, oxidizing

environment, and ash formation). However, these studies were conducted mainly under air combustion conditions and focused on co-combustion of sludge with coal or wood as the base fuel using BFB combustion technology [11–15].

CFB combustion technology has many advantages for heat recovery, so waste sewage sludge combustion should be retrofitted to, or newly commercialized for, CFB combustion facilities. In addition, a commercial FBC should be retrofitted to a carbon dioxide reduction facility. Only a few studies have been conducted on oxy-fuel combustion technology using CFB combustion technology for sludge combustion. When these technologies are applied to sludge combustion, combustion performances and the behavior of ash and heavy metals should be different under different combustion conditions. In this study, the particle size distributions composed of affluent metal components and the chemical reaction of aluminum, calcium, and potassium as alkali metals and chrome, copper, nickel, and zinc as tract metals from sludge combustion under the conditions of oxygen with nitrogen as the air combustion and oxygen with carbon dioxide as the oxy-fuel combustion were demonstrated, using a 30 kW CFB reactor.

2. Test Facility and Experimental Methods

2.1. Test Facility and Fuel Characteristics

Figure 1 shows a schematic stream of the test facility of the 30 kW CFB oxy-fuel reactor. The demonstration test was conducted in the facility, which consisted of a riser, a cyclone, a down-comer, and a loop-seal. The facility had a riser with an inner diameter of 0.15 m and a height of 6.4 m. The combustion temperature for the sludge fuel combustion was optimized at 800 °C. The feeding rate of the sludge was determined at 13 kg/h. Table 1 shows the summary of experimental conditions using the 30 kW CFB oxy-fuel reactor [16].



Figure 1. Schematic diagram of the 30 kW CFB oxy-fuel pilot test bed.

Design Factor	Value
Bed diameter (m)	0.15
Fuel feeding rate (kg/h)	13
Solid fuel mixing rate (%)	0~30
Oxygen injection rate (%)	23
Combustion temperature (°C)	800
Flow rate (L/min)	900

Table 1. Experimental conditions used during oxy-fuel combustion in the 30 kW CFB oxy-fuel pilot test bed.

2.2. Sampling and Analysis

The heating value of the sludge fuel was analyzed by an AC-350 calorimeter from the LECO Corporation in St. Joseph, MI, USA. The proximate analysis of sludge fuel was conducted by a TGA-601 from the LECO Corporation in MI, USA. The elemental analysis of sludge fuel was conducted by a 2400 series CHNS/O analyzer from Perkin Elmer Inc. in Waltham MA, USA. The analysis of the gaseous compounds in the outlet gas was conducted by PG-300 portable gas analyzer from HORIBA, Ltd in Kyoto, Japan. Particulate matter below 10 μ m in size, produced from the conditions of oxygen with nitrogen and oxygen with carbon dioxide, was sampled by a low-pressure impactor from Dekati Ltd. in Kangasala, Finland. Sludge fuel and particle samples were pretreated by means of the EPA 3050B method, and metal compounds in the sludge fuel and fine particulate matter were analyzed by an ICP-MS from Gilson Inc. in Middleton, WI, USA.

3. Results and Discussion

3.1. Combustion Surroundings and Flue Gas Composition

The pressure gradient in the reactor was investigated under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. Table 2 shows results of basic characteristic analysis of waste sewage sludge. In proximate analysis, waste sludge fuel contains much of volatiles and ashes. The calorific value was 3008 kcal/kg. In element analysis, carbon and hydrogen contents were 28.14 and 4.74, respectively. Chloride content was 530 ppm. In metal analysis, sludge fuel contained much of alkali metals and toxic heavy metals. Figure 2 shows the pressure and temperature profiles in the reactor under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. As shown in Figure 2a, the pressure gradient showed a typical pressure trend of the CFB at each point under both conditions of oxygen with nitrogen and oxygen with carbon dioxide. The decrease in pressure under the oxygen with nitrogen condition was higher than that under the oxygen with carbon dioxide condition. Table 3 shows the gas components of fluidization air. In a previous study, the drop in pressure under the oxygen with carbon dioxide condition with fluidized air, that consisted of carbon dioxide and oxygen, increased as the oxygen rate increased from 21% to 40%, because the kinematic viscosity of the fluidizing injection gas increased as the oxygen rate increased. The kinematic viscosity under the oxygen with nitrogen condition was larger than under the oxygen with carbon dioxide condition. The drop in pressure increased as the kinematic viscosity of fluidizing injection gas increased. As shown in Figure 2b, the temperature gradient in the reactor was uniform as the axis of height under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. In a previous study, the temperature gradient under the oxygen with nitrogen condition was relatively higher than under the 21% oxygen with carbon dioxide condition [9]. As shown in Table 3, the heat capacity of CO_2 was much larger than that of N_2 . It caused the flame temperature of the 21% oxygen with carbon dioxide condition to be lower than that of the oxygen with nitrogen condition since the fuel sludge had much volatile materials. It caused delayed devolatilization and delay in the ignition time of sludge fuel under the 21% of oxygen with carbon dioxide condition because much of the carbon dioxide was utilized, instead of nitrogen, on FBC combustion. However, the temperature gradient under the 23% of oxygen with carbon dioxide condition was higher than that of the 21% of oxygen with nitrogen condition. It was considered that the 23% of oxygen with carbon dioxide condition caused higher flame temperature than that of oxygen with nitrogen combustion, and devolatilization and total ignition time were fastly declined under the 23% oxygen condition. Table 4 shows the outlet gas temperature under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. Regarding flue gas temperature, the temperature was relatively higher under the oxygen with carbon dioxide condition than that under the oxygen with nitrogen condition. This was due to the fact that H₂O and CO₂ in the flue gas had larger heat capacity than N₂ and O₂, as shown in Table 3, and the temperature of the outlet gas, including more H₂O and CO₂, was larger than it was for typical air conditions. Furthermore, it was indicated that the sludge fuel had much volatiles, and the heat distribution from sludge fuel combustion was reached further along the CFB combustion system under the oxygen with carbon dioxide condition than that under the oxygen with nitrogen condition.

Proximate Analysis (wt, %)		Element Analysis (wt, %)		
Moisture	7.32	Carbon	28.14	
Volatile	45.11	Hydrogen	4.74	
Fixed carbon	12.25	Nitrogen	4.43	
Ash	35.04	Oxygen	23.90	
-	-	Sulfur	0.43	
Calorific value (kcal/kg)	3008	Chloride	0.053	
	Selected me	etals analysis		
Alkali metals ar	nalysis (ppm)	Toxic heavy metal	s analysis (ppm)	
Al	21,700.0	Zn	635.4	
Ca	11,204.7	Cu	305.2	
K	8249.0	Cr	42.5	
-	-	Ni	30.8	

Table 2. Results of basic characteristic analysis of waste sewage sludge.

Table 3. Physical gas properties of fluid flow utilized as fluidization air.

	H ₂ O	O ₂	N_2	CO ₂	Ratio, CO ₂ /N ₂
Density (ρ) [kg/m ³] Thormal	0.157	0.278	0.244	0.383	1.6
conductivity (k) [W/m·k]	0.136	0.087	0.082	0.097	1.2
Specific heat capacity (c _p) []/mol·°C]	45.67	36.08	34.18	57.83	1.7
Kinematic viscosity (m ² /s)	3.20	$2.09 imes 10^{-4}$	$2.00 imes 10^{-4}$	$1.31 imes 10^{-4}$	0.7

Table 4. Flue gas composition and temperature during the air and oxy-fuel combustion.

Test Condition	O ₂ (%)	CO ₂ (%)	CO (%)	Temp (°C)
Air	5.1	15.3	0.9	697.4
Oxy-fuel	6.4	82.9	1.5	736.9



Figure 2. The pressure and temperature profile from air and oxy-fuel combustion of waste sewage sludge: (**a**) pressure profile (**b**) temperature profile.

3.2. The Behavior of Ash and Heavy Metals

(1) Metal Composition of Bottom and Fly Ash

Sewage sludge consists of many volatiles, metal elements, and ash fractions. During sewage sludge combustion, metal elements undergo a series of reaction mechanisms, such as volatilization, nucleation, condensation, and coagulation for particulate formation [2,17]. These particulate formation mechanisms in bottom ash and fly ash under the oxygen with carbon dioxide condition were affected by different conditions in the combustion environment. Figure 3a shows the comparative concentration of alkali metals in the bottom ash and fly ash under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. The species of aluminum, calcium, and potassium were distributed mainly in the bottom and fly ash from sludge fuel combustion under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. The metal components tended to be associated with particle formation mechanisms by causing the growth of fly ash from sludge fuel combustion. In sludge fuel combustion, agglomeration and fouling are highly involved with calcium and alkali compounds, such as the chloride and sulfate species, which block the distribution of fluidizing air and heat exchange. Aluminum compounds are concerned with Cl-related corrosion, which arises mainly from the boiler of the sludge fuel combustion process. The Cl-related corrosion problem of Al compounds creates a serious problem for boilers and doubles the repair and operation costs of the sludge fuel combustion process. [18,19]. In bottom ash, the concentrations of alkali metals, such as aluminum, calcium, and potassium, under the oxygen with carbon dioxide condition were less than that under the oxygen with nitrogen condition. In fly ash, these metals showed a similar trend to that regarding the bottom ash under the oxygen with carbon dioxide condition. As shown, the concentrations of these metals in fly ash and bottom ash under the oxygen with carbon dioxide condition were lower than they were under the oxygen with nitrogen condition. It was indicated that the oxy-fuel combustion mitigated agglomeration, fouling, and corrosion problems from sludge fuel combustion, and was economically beneficial in terms of long-term operation of a sludge fuel combustion facility. In addition, oxy-fuel combustion for sewage sludge could contribute to a shorter ignition time of the metals and moderate particle growth in the bottom ash, which would temper de-fluidization by agglomeration, fouling, and corrosion in the CFB boiler. Figure 3b shows the comparative concentrations of heavy metals in the bottom and fly ashes under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. Chrome, nickel, copper and zinc were portioned mostly in the bottom and fly ashes from sludge combustion under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. Copper and zinc compounds in bottom ash and fly ash from sludge fuel combustion were less under the oxygen with carbon dioxide condition than that under the oxygen with nitrogen condition. In the oxygen with carbon dioxide condition, the gas circumstances were significantly different than under the oxygen with nitrogen condition. Lots of CO_2 under oxygen with the carbon dioxide condition had larger heat capacity than N_2 under the oxygen with nitrogen condition. Accordingly, CO₂ tended to take more heat in the condition of oxygen with carbon dioxide than the condition of oxygen with nitrogen condition, which caused decrease in combustion flame temperature. Eventually, a lower adiabatic temperature for oxy-fuel combustion occurred and caused a delay in ignition time, which delayed particle growth and formation, which was the pathway for the nucleation, vaporization, condensation, and coagulation mechanisms of those metals. However, an ignition delay would be rapidly declined over 23% of oxygen injection with decreased carbon dioxide rate for oxy-fuel combustion. Due to decreased carbon dioxide injection rate, the adiabatic flame temperature of this condition would be higher than it was for the air and 21% of oxygen injection rate for oxy-fuel combustion. As shown figure, the concentrations of alkali and heavy metals showed different trends for air and oxy-fuel combustion. The concentration of alkali metals, such as aluminum, calcium, and potassium in the fly ash under this condition were lower than they were under air combustion. Regarding heavy metals, the concentrations of zinc and copper compounds in the fly ash under this condition were lower than they were from

air combustion. Cr and Ni compounds in both ashes showed a different trend from the previously mentioned metals, with greater increase in ranges of oxy-fuel combustion than in air combustion. It was indicated that particle size distribution of fly ash should be changed along the air and oxy-fuel conditions because the different combustion surroundings and adiabatic flame temperatures likely affected the particle formation mechanisms from each metal compound in air and oxy-fuel conditions. Based on the test results, it was determined that oxy-fuel combustion was more efficient than air combustion in terms of heat recovery and economical operation by mitigating agglomeration, fouling, and corrosion problems from sewage sludge combustion.





(2) Particle Size Distribution and Mass Fraction of Metals

As sewage sludge combustion generates a large amount of fly ash, an understanding of particle size distribution of fly ash is important because it mainly consists of alkali and heavy metals. It was hypothesized that particle size distribution would be affected by different surroundings during air and oxy-fuel combustion. Figure 4 shows the particle size distribution in fly ash from air and oxy-fuel combustion of sewage sludge. Particle size distribution from air combustion was mainly accumulated by coarse particles over 2.5 μ m in size, whereas from oxy-fuel combustion, it showed each accumulation mode in fine particles below 1 μ m in size, super-micron particles ranging in size from 1 μ m to 2.5 μ m, and coarse particles over 2.5 μ m in size. Generally, fine particle formation was followed by a series of reactions of metal elements, such as nucleation, condensation, and coagulation. The sub-micron mode was depicted by each formation process, including direct vaporization of volatile metals and chemical reactions of refractory metal oxides. Refractory metal oxides (MO_X), in particular, could be reduced to sub-oxides (MO_{X-1}) by the reaction shown in Equation (1).

$$MO_{\chi} + CO \leftrightarrow MO_{\chi-1} + CO_2 \tag{1}$$

Figure 4. Particle size distribution in fly ash from air and oxy-fuel combustion of sewage sludge.

Sub-oxide metals were de-volatilized easily because of their low melting point, and then rapidly re-oxidized to gas phase to form fine particles, by a series of particle formation mechanisms, such as nucleation, volatilization, and condensation. The formation mechanism of a fine particle was dependent on fuel type, combustion temperature, and residence time. On the other hand, super-micron particles were formed from the following: (1) coalescence of the included mineral, which was not volatilized as a sub-oxide metal; (2) fine fragmentation of the excluded mineral; and (3) the solid to particle mechanism of inherent refractory metals that had high melting points. Coarse particles were formed from non-volatile mineral inclusions and char fragmentation. Figure 5 shows the mass fractions of the alkali and heavy metals mainly distributed in the fly ash from the combustion under the oxygen and nitrogen condition compared to the distribution under the oxygen and carbon dioxide condition. Aluminum, calcium and potassium were largely contained in the particle size between 1 μ m and 2.5 μ m under the conditions of oxygen with nitrogen and oxygen with carbon dioxide. In general, the size of the particles was directly generated from the metals inherent to sludge combustion. These metals were inherently refractory metals in fuel, and the particles were generated by the mechanisms of solid to particle, including those of inherently refractory metals. Fine particles were also generated by particle formation mechanisms, such as vaporization, nucleation, and condensation. The aluminum, calcium and potassium showed significant accumulation

trend between 1 μ m and 2.5 μ m from the combustion of oxygen with nitrogen and oxygen with carbon dioxide. Generally, potassium tended to be much volatilized, which generated fine particles below 1 µm by particle generation mechanisms, such as vaporization and condensation. On the other hand, potassium also formed super-micron particles, larger than 1 μ m. It was considered that metal vapor would spread on ash materials by chemical mechanisms, combine to aluminum and calcium, and finally cause conglomeration of particles. Under the oxygen with carbon dioxide combustion, the portion of aluminum, calcium and potassium were better conglomerated as fine particles below 1 μ m than under oxygen with nitrogen combustion. The portions of aluminum, calcium and potassium under the oxygen with carbon dioxide condition, between 1 μ m and 2.5 μ m in size, were a bit larger than those under the oxygen with nitrogen condition, whereas the portion of aluminum, calcium and potassium under the oxygen with nitrogen condition, over $2.5 \,\mu$ m, were larger than those under the oxygen with carbon dioxide condition. This was explained by the fact that the ignition time delay under the oxygen with carbon dioxide condition was more rapid than that under the oxygen with nitrogen condition, and fine particle formation from aluminum, calcium and potassium was elevated by physical and chemical reactions. Fine particle formation from heavy metals, such as chrome, nickel, copper, and zinc, was conducted more intensively under the oxygen with carbon dioxide condition than that under the oxygen with nitrogen condition. It was considered that the fine particle formation from the oxygen with carbon dioxide condition was more intensive than that from the oxygen with nitrogen condition. The fine particles could be formed by the chemical reaction of the metal oxides. In general, the metal oxides could be changed into sub-oxide compounds when the original metal oxide reacted with carbon monoxide. The sub-oxide compounds were easily volatilized because of low melting temperature. Finally, because of the large amount of carbon dioxide, the vapor of the compounds could be more intensively re-oxidized to generate fine particles under the oxygen with carbon dioxide condition than those under the oxygen with nitrogen condition. Fine particle formation from zinc and copper would occur by volatilization and condensation, because the melting temperature of the compounds was lower than the adiabatic flame temperature under both conditions. On the other hand, the melting temperature of chrome and nickel was much higher. Finally, chrome and nickel mainly formulated in coarse particles, over $2.5 \,\mu$ m, under the oxygen and nitrogen condition.









Figure 5. Mass fractions of alkali and heavy metals from air and oxy-fuel combustion: (**a**) alkali metals, (**b**) trace metals.

4. Conclusions

The comparative study on the behavior of alkali and heavy metals from waste sludge combustion under air and oxy-fuel conditions was conducted using a 30 kW CFB pilot test bed. Based on the experimental results, the major results are summarized as follows:

- 1. Temperature and pressure profiles in air and oxy-fuel combustion of sewage sludge were different according to mixtures of O_2/CO_2 and O_2/N_2 . It was indicated that combustion surroundings for CFB waste sludge combustion changed due to physical gas properties, such as kinematic viscosity, density, and heat capacity of nitrogen, oxygen, and carbon dioxide during air and oxy-fuel combustion.
- 2. Based on flue gas and ash composition analysis in air and oxy-fuel combustion, the oxy-fuel combustion was more efficient than air combustion in terms of heat recovery, beneficial carbon dioxide capture, and economical long-term operation by mitigating agglomeration, fouling, and corrosion problems from sewage sludge combustion.
- 3. The PSD in fly ash under the oxygen with nitrogen condition was mainly distributed as coarse particles over $2.5 \ \mu m$, whereas that under the oxygen with carbon dioxide plotted each peak mode as ultra-fine particle below 1 μm and fine particle between 1 μm and 2.5 μm . The results were caused by each series of mechanisms by metal compounds under different circumstances in both combustion conditions.
- 4. The portions of alkali metals under the oxygen with carbon dioxide condition were below 2.5 μm a bit larger than those under the oxygen with nitrogen condition. It is explained that the ignition time delay under the oxygen with carbon dioxide condition was more rapid than that under the oxygen with nitrogen condition. and fine particle formation from the metals was elevated by volatilization and condensation reactions.
- 5. Fine particle formation from chrome, nickel, copper, and zinc was more intensively conducted under the oxygen with carbon dioxide condition than under the oxygen with nitrogen condition. This was because of the large amount of carbon dioxide, and the compounds vapor could be more intensively re-oxidized to generate fine particles under the oxygen with carbon dioxide condition than those under the oxygen with nitrogen condition.

Author Contributions: Conceptualization, H.-N.J. and H.S.C.; methodology, H.-N.J.; software, H.-N.J.; validation, H.-N.J., H.-M.Y. and H.S.C.; formal analysis, H.-M.Y.; investigation, H.-M.Y.; resources, H.-M.Y.; data curation, H.-M.Y.; writing—original draft preparation, H.-N.J.; writing—review and editing, H.-N.J. and H.S.C.; visualization, H.-N.J.; supervision, H.S.C.; project administration, H.S.C.; funding acquisition, H.S.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: This work was supported by the Korea Ministry of Environment as the Field of Green Financing on Green Integration Human Resource Development Project. Also, This study was carried out with the support of 'R&D Program for Forest Science Technology (Project No. 2021356A00-2223-AC03)' provided by Korea Forest Service(Korea Forestry Promotion Institute).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Buhre, B.; Elliott, L.; Sheng, C.; Gupta, R.; Wall, T. Oxy-fuel combustion technology for coal-fired power generation. *Prog. Energy Combust. Sci.* 2005, 31, 283–307. [CrossRef]
- Toftegaard, M.B.; Brix, J.; Jensen, P.A.; Glarborg, P.; Glarborg, A.D. Oxy-fuel combustion of solid fuels. *Prog. Energy Combust. Sci.* 2010, 36, 581–625. [CrossRef]
- Rink, K.K.; Kozinski, J.A.; Lighty, J.S. Biosludge incineration in FBCs: Behavior of ash particles. Combust. Flame 1995, 100, 121–130. [CrossRef]
- 4. Cenni, R.; Frandsen, F.; Gerhardt, T.; Spliethoff, H.; Hein, K. Study on trace metal partitioning in pulverized combustion of bituminous coal and dry sewage sludge. *Waste Manag.* **1998**, *18*, 433–444. [CrossRef]
- 5. Latva-Somppi, J.; Kauppinen, E.; Valmari, T.; Ahonen, P.; Gurav, A.S.; Kodas, T.T.; Johanson, B. The ash formation during co-combustion of wood and sludge in industrial fluidized bed boilers. *Fuel Process. Technol.* **1998**, *54*, 79–94. [CrossRef]

- 6. Lopez, M.H.; Abelha, P.; Lapa, N.; Oliveira, J.S.; Cabrita, I.; Gulyurtlu, I. The behavior of ashes and heavy metals during the co-combustion of sewage sludge in a fluidized bed. *Waste Manag.* **2003**, *23*, 859–870.
- Marani, D.; Braguglia, C.M.; Mininni, G.; Maccioni, F. Behaviour of Cd, Cr, Mn, Ni, Pb, and Zn in sewage sludge incineration by fluidized bed furnace. *Waste Manag.* 2003, 23, 117–124. [CrossRef] [PubMed]
- Åmand, L.-E.; Leckner, B. Metal emissions from co-combustion of sewage sludge and coal/wood in fluidized bed. *Fuel* 2004, *83*, 1803–1821. [CrossRef]
- 9. Elled, A.L.; Amand, L.E.; Leckner, B.; Andersson, B.A. Influence of phosphorus on sulphur capture during co-firing of sewage sludge with wood or bark in a fluidized bed. *Fuel* **2006**, *85*, 1671–1678. [CrossRef]
- 10. Elled, A.L.; Amand, L.E.; Leckner, B.; Andersson, B.A. The fate of trace elements in fluidized bed combustion of sewage sludge and wood. *Fuel* 2007, *86*, 843–852. [CrossRef]
- 11. Van de Velden, M.; Dewil, R.; Baeyens, J.; Josson, L.; Lanssens, P. The distribution of heavy metals during fluidized bed combustion of sludge (FBSC). *J. Hazard. Mater.* 2008, 151, 96–102. [CrossRef]
- 12. Barbosa, R.; Lapa, N.; Boavida, D.; Lopes, H.; Gulyurtlu, I.; Mendes, B. Co-combustion of coal and sewage sludge: Chemical and ecotoxicological properties of ashes. *J. Hazard. Mater.* **2009**, 170, 902–909. [CrossRef] [PubMed]
- Solimene, R.; Urciuolo, M.; Cammarota, A.; Chirone, R.; Salatino, P.; Damonte, G.; Donati, C.; Puglisi, G. Devolatilization and ash comminution of two different sewage sludges under fluidized bed combustion conditions. *Exp. Therm. Fluid Sci.* 2010, 34, 387–395. [CrossRef]
- 14. Lopez, H.; Gulyurtlu, I.; Abelha, P.; Crujeira, T.; Salema, D.; Freire, M.; Pereira, R.; Cabrita, I. Particulate and PCDD/F emissions from coal co-firing with solid biofuels in a bubbling fluidized bed reactor. *Fuel* **2009**, *88*, 2373–2384. [CrossRef]
- 15. Urciuolo, M.; Solimene, R.; Chirone, R.; Salatino, P. Fluidized bed combustion and fragmentation of wet sewage sludge. *Exp. Therm. Fluid Sci.* **2012**, *43*, 97–104. [CrossRef]
- Jang, H.-N.; Kim, J.-H.; Back, S.-K.; Sung, J.-H.; Yoo, H.-M.; Choi, H.S.; Seo, Y.-C. Combustion characteristics of waste sludge at air and oxy-fuel combustion conditions in a circulating fluidized bed reactor. *Fuel* 2015, 170, 92–99. [CrossRef]
- 17. Fryda, L.; Sobrino, C.; Cieplik, M.; van de Kamp, W. Study on ash deposition under oxyfuel combustion of coal/biomass blends. *Fuel* **2010**, *89*, 1889–1902. [CrossRef]
- Wu, Y.; Wang, C.; Tan, Y.; Jia, L.; Anthony, E.J. Characterization of ashes from a 100 kWth pilot-scale circulating fluidized bed with oxy-fuel combustion. *Appl. Energy* 2011, *88*, 2940–2948. [CrossRef]
- 19. Fryda, L.; Sobrino, C.; Glazer, M.; Bertrand, C.; Cieplik, M. Study of ash deposition during coal combustion under oxyfuel conditions. *Fuel* **2012**, *92*, 308–317. [CrossRef]

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