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Review

Aluminosilicate Clay Minerals: Kaolin, Bentonite, and Halloysite as Fuel Additives for Thermal Conversion of Biomass and Waste

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Abstract: The current focus on renewable energy sources and the circular economy favors the thermal conversion of low-quality fuels, such as biomass and waste. However, the main limitation of their usability in the power sector is the risk of slagging, fouling, ash deposition, and high-temperature corrosion. These problems may be avoided or significantly mitigated by the application of aluminosilicate clay minerals as fuel additives. In this paper, the three most commonly occurring aluminosilicates are reviewed: kaolin, halloysite, and bentonite. Their application has been proven to minimize combustion-related problems by bonding alkalis in high-melting compounds, thus increasing ash melting temperatures, reducing ash deposition tendencies, and decreasing the particulate matter emission. Due to excellent sorption properties, aluminosilicates are also expected to fix heavy metals in ash and therefore decrease their emissions into the atmosphere. The application of aluminosilicates as fuel additives may be a key factor that increases the attractiveness of biomass and other low-quality fuels for the power sector.

Keywords: biomass; fuel; renewable energy; waste-to-energy; kaolin; halloysite; bentonite; aluminosilicate; wheat straw; miscanthus

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1. Introduction

The depletion of fossil fuels and their adverse impact on the environment, along with the unstable situation in the global energy market, has resulted in a growing interest in alternative energy sources. As presented in Table 1, the share of fossil fuels in global primary energy consumption declined from 85.9% in 2015 to 83.1% in 2020 with the simultaneous rise of renewable energy sources from 3.3% to 5.7%. Among the renewables, biomass plays a significant role as it is considered a sustainable, flexible fuel that can be used in both developed and developing countries for the transition to a low-carbon economy [1,2]. At the same time, the general amount of waste produced worldwide is growing together with economic growth and industrialization [3,4]. The total global production of waste has reached seven to nine billion tonnes per year [5], including two billion tonnes of municipal solid waste (MSW) [6]. Since not all waste can be recycled, thermal treatment is considered a sustainable method for managing mixed, contaminated, and residual MSW [7–9] as it provides both material utilization and energy recovery [10–12].

Table 1. Primary energy consumption in the world in 2015 and 2020 [13].

Energy Source	Primary Energy Consumption in the World			
	2015		2020	
	EJ	%	EJ	%
	Fossil fuels			
Oil	183.63	33.7	173.73	31.2
Natural Gas	125.22	23	137.62	24.7
Coal	158.64	29.1	151.42	27.2
Total fossil	467.49	85.9	462.77	83.1
	Non-Fossil fuels			
Nuclear	23.46	4.3	23.98	4.3
Hydro	35.38	6.5	38.16	6.9
Renewable	18.1	3.3	31.71	5.7
Total non-fossil	76.94	14.1	93.85	16.9
Total all sources	544.43	100.0	556.62	100.0

Aside from unquestionable benefits, biomass and waste may be considered low-quality fuels, whose specific properties limit their usability in the power sector. The limitations are directly associated with the chemical composition of biomass and waste, most importantly the elevated contents of chlorine (Cl), sodium (Na), and potassium (K), resulting in low ash fusion temperatures (AFTs) [14–17]. Some types of farming residues may be characterized by an extreme chlorine content of above 10% [18]. Similar Cl concentrations may occur in waste since plastic and biowaste, the two main chlorine sources in MSW, comprise the main fractions of mixed waste collected from households [19]. The presence of chlorine leads to the formation of low-melting mixtures containing metal chlorides and, thus, to high-temperature corrosion through the multi-step active oxidation process [20]. Chlorine and alkalis tend to merge with silica, which occurs in the ash mainly as silica (SiO_2), and reduce the fluid temperatures from approximately 1700 °C (melting point of SiO_2) to approximately 750 °C. As a result of such a process, the AFTs of biomass and waste are usually lower than those of typical coals; for instance, the initial deformation temperature of biomass ash can be as low as 700 °C [21]. Such low melting tendencies lead directly to issues such as formation of deposits on heating surfaces of a boiler, slagging, fouling, high-temperature corrosion, bed agglomeration (defluidization) in circulating fluidized bed (CFB), boilers, and increased particulate matter (PM) emission [22–29], as clearly indicated by both experimental research and industrial experience [30–33]. These issues are not specific to biomass and waste but are likely to occur during the combustion of low-rank coals, as well.

Several methods for the reduction of the above problems, such as fuel mixing (blending), washing (leaching out) the unwanted elements, and the use of fuel additives have been investigated [34–38]. Among the additives, four main groups can be determined [39,40]:

- Aluminosilicates-based additives;
- Calcium-based additives;
- Sulphur-based additives;
- Phosphorous additives.

Among these groups, aluminosilicate clays seem particularly promising, as they are easy to handle, commonly occurring natural minerals. Their application as fuel additives may be an environmental-friendly and cost-effective remedy for operational issues of low-quality fuels. Their presence is expected to improve the ash characteristics, prevent corrosion damages, reduce particulate matter emission, and capture heavy metals in the ash. Despite the unquestionable benefits of aluminosilicates application, there is no comprehensive literature review on this field. According to the authors' best knowledge, the available data tend to elaborate all groups of additives, and not enough attention is paid to the latest findings on aluminosilicates. Therefore, the presented paper aims to systematize

the literature data concerning aluminosilicate clays and their possible application in the power sector. The three most commonly used minerals are under consideration in this study: kaolin, bentonite, and halloysite.

2. Characteristics of Aluminosilicate Clay Minerals

Aluminosilicate clay minerals belong to the kaolinite-serpentine subgroup and are described by the general chemical formula $Al_2Si_2O_5(OH)_4$. They are characterized by electroneutral layered structures with tetrahedral and octahedral sheets held together by water molecules or secondary forces such as hydrogen bonding [41]. Despite kaolin, halloysite, and bentonite, other clays such as dickite and nacrite also belong to this subgroup; however, they are less popular among industrial users. Industrial interest in kaolin, halloysite, and bentonite results from their large deposits located in Poland, as well as many other countries in the world [42,43] (Figure 1).

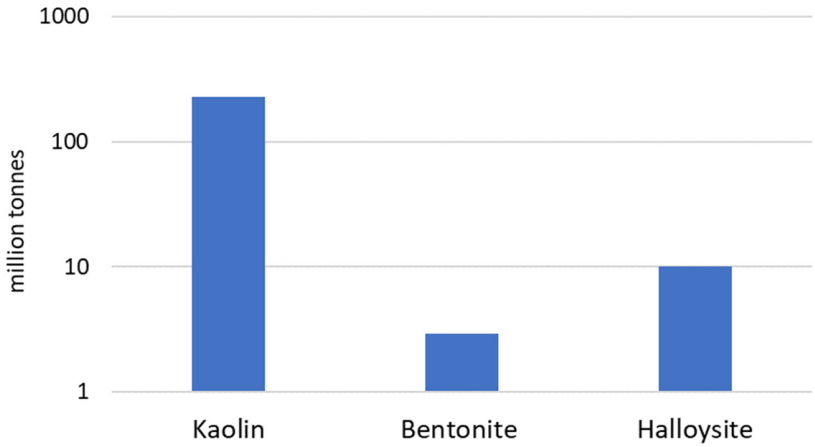


Figure 1. Aluminosilicate clay minerals deposits in Poland [43].

Aluminosilicates are suitable for diverse industrial applications, presented in Figure 2. They are commonly used as feedstock for the ceramic, chemical, and paper industries [44]. Due to their predisposition for high adsorption, they can be used as sorbents for petrochemicals, as catalysts, in cosmetics, or as dietary supplements for cattle [45,46]. Their latest application paths are composite materials [47] and biomedicine [48,49].

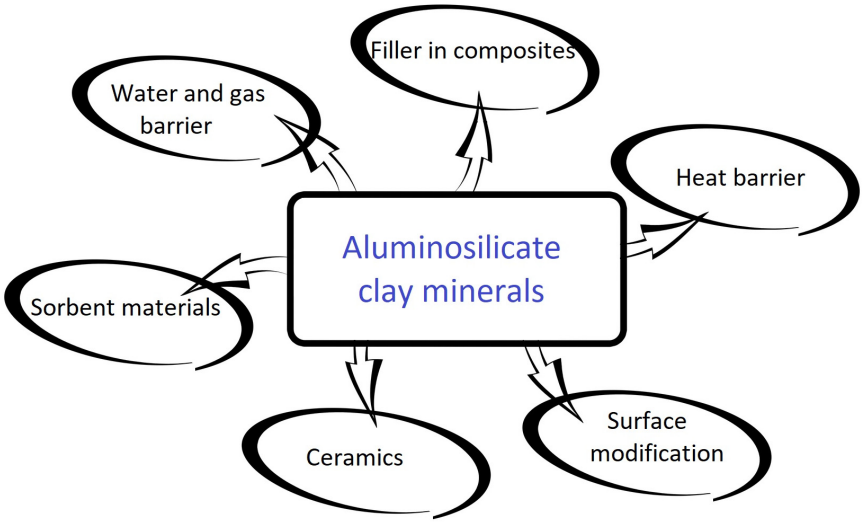
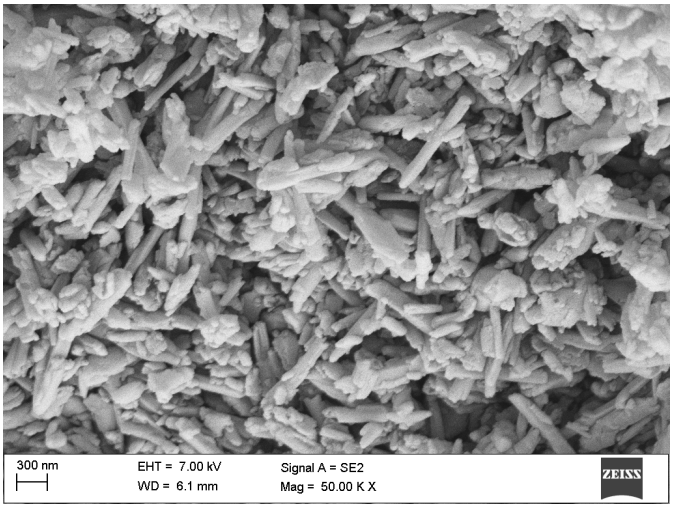


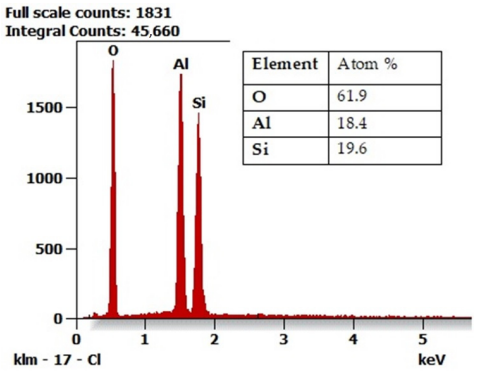
Figure 2. Common applications of aluminosilicate clay minerals.

Aluminosilicates can be considered excellent fuel additives since they meet all the specific requirements: they are characterized by high porosity and high specific surface, high reactivity, high melting points, and non-toxicity [50,51]. They are claimed to have no negative influence on the combustion process, which means they do not lower the combustion efficiency or favor the formation of any pollutants [52,53]. Their chemical stability and powdery structure make them easy to transport, store, and apply. They are characterized by low operational costs, as they occur commonly around the world, and do not require advanced pre-processing before use [42].

2.1. Halloysite

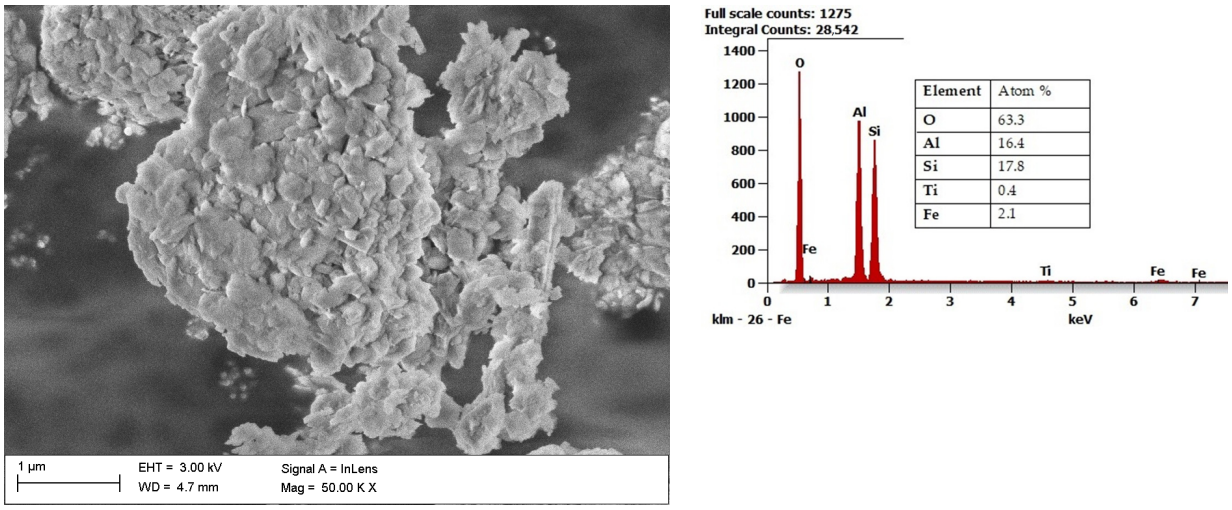
Halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) draws the researchers' attention due to its unique structure. Microstructural and nanostructural analysis of various halloysite samples revealed either the dominance of halloysite nanoplates (HNP), a mix of halloysite nanoplates and halloysite nanotubes (HNT), or predominantly nanotubular structure [54]. The mixed structure of halloysite consisting of both HNP and HNT is presented in Figure 3a with its chemical composition. Halloysite nanotubes are composed of two layers with mostly a hollow, slender cylindrical structure in the submicron ambit [55,56]. Among other minerals in its group, halloysite features a higher value of the specific surface area (60–80 m^2/g) than the surface area of kaolin (3–12 m^2/g) and the high porosity of structure. Therefore, composite materials using halloysite are becoming increasingly popular, a fascinating application of which is polyaniline-halloysite nano clay hybrid composites that can produce sensors and corrosion-resistant coatings [57]. Another potential application of halloysite is its use as a reinforcement in composites based on soy protein/basil seed gum used for the production of food packaging [58]. Finally, the potential use of halloysite also concerns materials limiting the growth of Escherichia coli bacteria [59]. Halloysite from European deposits (Figure 3b) may consist of some impurifications, mainly iron oxides, which can be considered beneficial in terms of catalytic properties [60]. The unique structural characteristics of halloysite make it the best prospective fuel additive among those considered in this study.





(**a**)

Figure 3. *Cont.*



(**b**)

Figure 3. Scanning electron microscope (SEM) image of halloysite from USA together with results of the chemical composition analysis obtained using the Energy-dispersive (EDS) X-ray characteristic (**a**), SEM image of halloysite from Europe, together with results of the chemical composition analysis obtained using the EDS X-ray characteristic (**b**).

2.2. Kaolin

Another aluminosilicate mineral is kaolin, with a chemical composition of $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one sheet of silica tetrahedron SiO_4^{4-} through small atoms with one sheet of alumina octahedron $Al(OH)_6^{3-}$. As presented in Figure 4, it features a predominantly plate structure. Kaolin is, among all types of clay, defined as the least reactive one since it is characterized by a relatively small specific surface (3–12 m^2/g) [61]. When heated, kaolin is transformed into metakaolin and further into quartz and mullite [62]. Kaolin-based slurries have a wide range of applications, such as diaphragm walls, drilling fluids, adhesives, cosmetics, refractories, and pharmaceuticals, due to their abundance in nature, low cost, and lack of swelling [63]. An increasingly popular application of kaolin is its use as an additive to composites, mainly based on polymers and biopolymers [64,65].

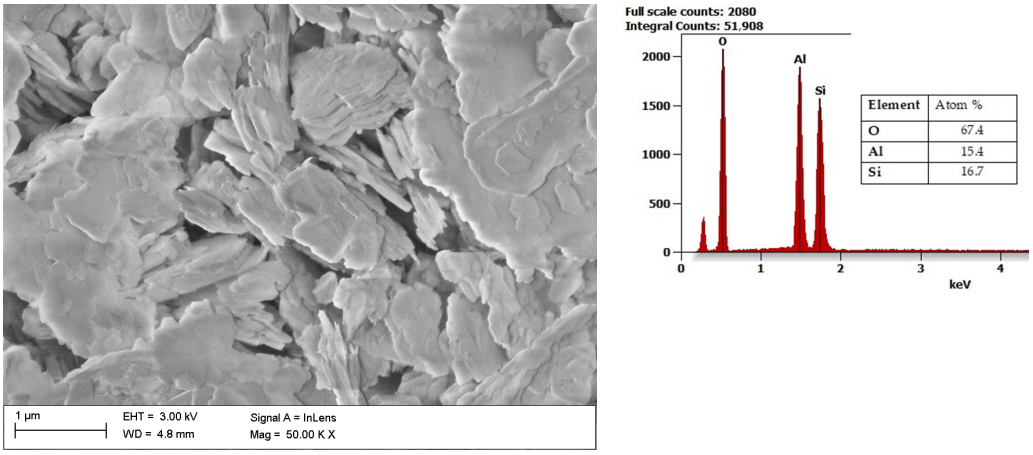


Figure 4. SEM image of Kaolin together with results of the chemical composition analysis obtained using the EDS X-ray characteristic.

2.3. Bentonite

A widely studied member of the aluminosilicates group is bentonite, which can be characterized as an absorbent swelling clay consisting mainly of montmorillonite. In

addition, there is bentonite, in which there is a Na- or Ca-based montmorillonite. Similar to kaolin, bentonite features a plate structure, as presented in Figure 5. One of the main applications of bentonite is its use in the production of barrier materials [66]. The volume of the bentonite can increase several times after swelling, reducing the volume of the flow channels. Compared to other materials of this type, bentonite barriers are characterized by lower permeability and costs. Therefore, in recent years, various bentonite barriers have been developed and used [67]. The latest research focuses on the potential use of bentonite for filtration and sealing water and gas extraction processes, especially at high temperatures [68].

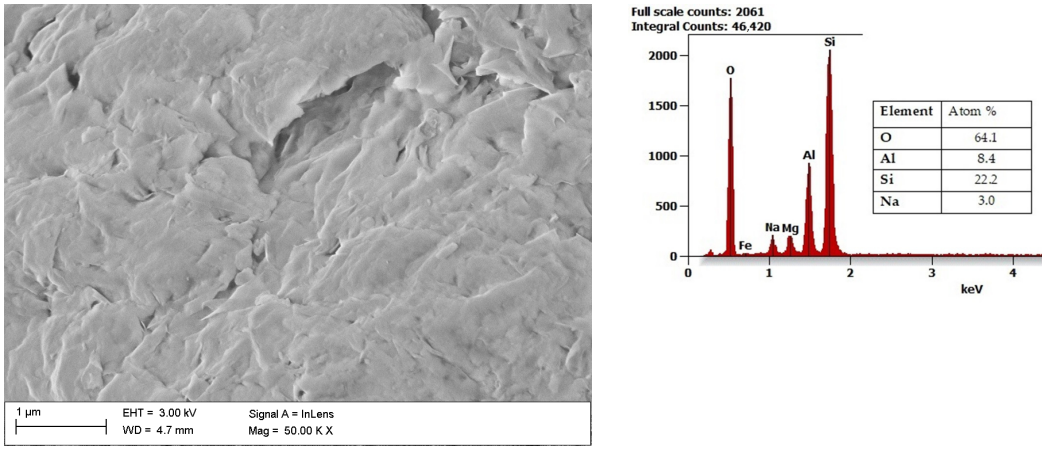


Figure 5. SEM image of bentonite with results of the chemical composition analysis obtained using the EDS X-ray characteristic.

3. Mitigation of Combustion-Related Problems

Aluminosilicates, when used as fuel additives, affect ash characteristics by bonding potassium and sodium in forms with high melting points while chlorine is released as hydrogen chloride (HCl) [23,69]. According to reactions 1 and 2, aluminosilicates react with potassium chloride (KCl), whose melting point is 770 °C, and form kalsilite ($KAlSiO_4$) and leucite ($KAlSi_2O_6$)—compounds with melting points of above 1600 °C and 1500 °C, respectively. Aluminosilicates also react with other potassium compounds, such as potassium sulfate (K_2SO_4) and potassium carbonate (K_2CO_3) according to reactions 3 and 4. Due to the high specific surface area, aluminosilicates may also adsorb alkali metals on their surface, thus the process of bonding alkalis is expected to be multi-staged and start at a low temperature range [70].

$$Al_2O_3{\cdot}2SiO_2(s) + 2KCl(g) + H_2O(g) \rightarrow 2KAlSiO_4(s,l) + 2HCl(g) \quad (1)$$

$$Al_2O_3{\cdot}2SiO_2(s) + 2SiO_2(s) + 2KCl(g) + H_2O(g) \rightarrow 2KAlSi_2O_6(s,l) + 2HCl(g) \quad (2)$$

$$Al_2Si_2O_5(OH)_4(s) + K_2SO_4(g) \rightarrow 2KAlSiO_4(s,l) + 2H_2O(g) + SO_3(g) \quad (3)$$

$$Al_2Si_2O_5(OH)_4(s) + K_2CO_3(g) \rightarrow 2KAlSiO_4(s,l) + 2H_2O(g) + CO_2(g) \quad (4)$$

In practical terms, the introduction of aluminosilicates into the combustion process is expected to reduce ash deposition and bed agglomeration in fluidized beds, as well as slagging and fouling of boiler heating surfaces. Moreover, aluminosilicates may reduce the risk of high-temperature (chlorine-induced) corrosion by reducing the amount of KCl in ash deposits.

3.1. The Influence of Aluminosilicate Clay Minerals on Potassium Retention

In recent years years, aluminosilicates have become a subject of interest as fuel additives for biomass and low-quality coals, and a group of research focuses on their influence on potassium compounds transformation. Agricultural biomass (bagasse and eucalypt bark) doped with kaolin was investigated by Liao et al. [71] in both laboratory and pilot scales. Kaolin was proven to have high efficiency in bonding potassium in the form of $KAlSi_2O_6$, while chlorine was released in a form of HCl. Hardy et al. [72] tested halloysite, kaolin, and bentonite in comparison with fly ash as fuel additives during agricultural biomass co-combustion. As a result, halloysite and kaolin were proven to be most efficient in bonding potassium in the high-melting compounds, together with chlorine release. Similarly, Clery et al. [73] investigated three biomass types (softwood, wheat straw, and olive residue) with an aluminosilicate-based additive and determined its positive influence on the potassium compounds' transformation. In the absence of the additive, the loss of K at the elevated temperature was determined to be 40–80% while, in the presence of the additive, up to 100% of K was retained in the ash. In the research by Dragutinovic et al. [74], kaolin was found to be an efficient K sorbent whose presence led to the formation of K-Al, K-Mg, Ca-Mg, and K-Al silicates in the ash during the combustion of crop residues (corn stover, corn cobs, wheat straw, and their blends).

3.2. The Influence of Aluminosilicate Clay Minerals on Ash Fusion Temperatures and Deposition Tendency

As a result of the formation of high-melting compounds, the characteristic ash fusion temperatures of biomass can be elevated and reach the values typical for coals, according to the data presented in Table 2. In the research by Mroczek et al. [75], the halloysite addition caused an increase in the ash softening temperature of wheat straw and pelletized sunflower husk from 960 to 1080 and from 900 to 1070 °C, respectively, and the ash melting temperature from 1180 to 1240 and from 1110 to 1210 °C, respectively. Similarly, Roberts et al. [76] observed an increase in the initial deformation temperature of olive cake from 935 to 1135 °C and flow temperature from 1325 to 1500 °C as a result of kaolin addition. Sobieraj et al. [77] investigated several biomass types with halloysite addition and concluded that the addition of halloysite affects the increase of characteristic ash fusion temperatures from 20 °C up to 270 °C but usually from 50 °C to 150 °C, depending on the additive dose.

Table 2. The influence of aluminosilicates on ash fusion temperatures (AFTs) of biomass.

Fuel	Additive	AFT Change	Standard Used	Reference
Wheat straw	Halloysite 1 wt.%	Sintering temperature from 840 to 850 °C Softening temperature from 960 to 1080 °C Melting temperature from 1180 to 1240 °C	PN-G-04535:1982	[75]
Sunflower husk	Halloysite 1 wt.%	Sintering temperature from 810 to 900 °C Softening temperature from 900 to 1070 °C Melting temperature from 1110 to 1210 °C	PN-G-04535:1982	[75]
Wheat-rye straw	Halloysite 2 wt.%	Shrinkage starting temperature from 750 to 860 °C Initial deformation temperature from 960 to 1030 °C Hemispherical temperature from 1070 to 1220 °C Fluid temperature from 1170 to 1260 °C	CEN/TS 15370-1:2007	[77]
Miscanthus	Halloysite 4 wt.%	Shrinkage starting temperature from 780 to 930 °C Initial deformation temperature from 940 to 1210 °C Hemispherical temperature from 1170 to 1260 °C Flow temperature from 1260 to 1270 °C	CEN/TS 15370-1:2007	[77]
Olive cake	Kaolin 5 wt.%	Initial deformation temperature from 935 to 1135 °C Softening temperature from 1290 to 1445 °C Fluid temperature from 1325 to 1500 °C	ASTM D1857	[76]
White wood	Kaolin 5 wt.%	Initial deformation temperature from 1075 to 927.5 °C Softening temperature from 1275 to above 1585 °C Fluid temperature from 1290 to above 1585 °C	ASTM D1857	[76]

The effects of kaolin addition on the formation of deposits on the heating surface during the combustion of high-Na/Ca coal were investigated by Hui et al. [78]. The presence of kaolin changed the dominant compounds of fly ash to high-melting minerals such as $CaSiO_3$, $CaSO_4$, $Ca_2MgSi_2O_7$, and $NaCaAlSi_2O_7$, resulting in a lower deposition rate than raw coal. The presence of aluminosilicates in ash deposits was indicated as the crucial factor in the mitigation of chlorine-induced corrosion during the combustion of chlorine-rich refuse derived fuel (RDF), and halloysite was found to be a more efficient additive than either kaolin or sulfur [79].

3.3. Aluminosilicate Clay Minerals in Fluidized Bed Combustion

When it comes to combustion in fluidized beds, kaolin and halloysite were investigated by Zuwała et al. [80] as additives for different biomass blends (willow chips, corn straw chips, and sunflower husks). The research was carried out in bubbling fluidized-bed combustors on both laboratory and industrial scales. Halloysite and kaolin were found to be more efficient remedies for the defluidization process than the limestone and desulfurization residues, also investigated in this study. Similarly, kaolin was proven to prevent bed defluidization by Morris et al. [81] during the combustion of miscanthus. According to the SEM/EDX analysis of agglomerates, the evident chemical reactions between kaolin and fuel occurred as potassium was found to migrate into the kaolin particle at depths of up to 60 µm. In the study by Nguyen et al. [82], kaolin was investigated to manage ash problems during oxy-biomass combustion in a 0.1 MWth circulating fluidized bed facility. The results revealed that potassium capture performance was improved by up to 24% at the mass ratio of kaolin/wood pellet equal to 0.25. The content of $KAlSiO_4$ in the ash increased as a result of the adsorption of gaseous potassium on the metakaolin surface. The fouling tendency of ash and SO_2 emission decreased with a stable combustion efficiency of over 99%.

3.4. The Influence of Aluminosilicate Clay Minerals on Particulate Matter Emission

Another important goal of aluminosilicates is the reduction of the formation and emission of particulate matter (PM) by bonding aerosol-forming elements, mostly K, Al, Cl, S, and Zn, in the bottom ash [40,83]. The addition of kaolin (1.5 wt.%) to the combustion of corn cob pellets resulted in approximately 48 wt.% reduction in the emission of total particulate matter by fixing the volatile alkali metals (K and Al) in high-temperature-stable silicates [84]. Moreover, ash examination revealed a lower sintering tendency. Similarly, Hofer et al. [85] showed that the addition of 1 wt.% of kaolin resulted in a reduction of K in the inorganic particulate matter emitted during the spruce wood and miscanthus combustion by 55% and by 78%, respectively. Kaolin and limestone were investigated in terms of the reduction of the emission of particulate matter with particle size below 1 µm (PM_1) during pulverized coal combustion in an O_2/CO_2 atmosphere [86]. The results show that the emissions of PM_1 were reduced effectively by either kaolin or limestone since kaolin has the capability to capture Na and K vapors, whereas limestone reacts with sulfur. The blended additive made of kaolin and limestone was tested by Liu et al. [87] during the combustion of coal in a 1000 MW power station and was found to diminish the mass concentrations of the ultrafine PM and $PM_{2.5}$ by 29.77% and 40.91% respectively.

3.5. Other Fuel-Related Applications of Aluminosilicate Clay Minerals

Aluminosilicate clay minerals can also be applied as catalysts for thermocatalytic conversion. When applied to the pyrolysis process, they improve the product yields, allow obtaining liquid products of the required hydrocarbon range, and reduce tar formation. The comprehensive review of the thermocatalytic conversion of plastics over clays has already been summarized by Seliverstov et al. [88] and Fadillah et al. [89]. In some of the works reviewed, kaolin was found to act as a catalyst during the pyrolysis of different plastic feedstocks: virgin high-density polyethylene (HDPE), HDPE waste, and mixed plastic waste (MPW) by Auxilio et al. [90]. Similarly, Abnisa [91] investigated the pyrolysis of mixed plastic waste with the addition of 5% of bentonite, which was found to promote

liquid product formation, reduce gas yield, and significantly minimize tar residue. Oil produced with bentonite added not only produced higher yields but better physical properties, as well, compared to the oil produced with zeolite. The highest liquid yields of 100 wt.% for HDPE pyrolysis over bentonite (50 wt.%) and spent fluid catalytic cracking catalyst (FCC) were obtained by Elordi et al. [92], and 99.82 wt.% for pyrolysis of low-density polyethylene (LDPE) on neat kaolin powder were obtained by Erawati et al. [93]. The reviewed research reveals that Seliverstov et al. [88] concluded that the modification of clay minerals (e.g., acid-washing or pillaring) was helpful to achieve a higher yield of the liquid fraction in some reviewed cases, but in others, pure clays also showed excellent catalytic activity.

Moreover, the addition of aluminosilicate minerals may positively influence the long-term storage of biomass, as halloysite was proven to suppress the formation of mycotoxins [94].

4. Mitigation of the Heavy Metals Emission

Due to high sorption properties, aluminosilicates are expected to fix metals in ash, thus reducing their emission in the flue gas. In research by Szul et al. [95], the performance of additives on the high-temperature sorption of elements such as Cr, Mn, Mo, Ni, and Zn was investigated, and halloysite was demonstrated to have better overall efficiency than kaolin, dolomite, and chalk. Du et al. [96] tested kaolin as an additive during high-organic solid waste pyrolysis and found its high adsorption capacity for Cd, Cr, Pb, Cr, Cu, Pb, and Zn. Wang et al. [97] determined kaolin injection into the combustion zone to be an effective remedy to control submicron Pb emission over the temperature range from 850 °C to 900 °C and kaolin pre-mixed with the fuels as more effective at the temperature of 950 °C. A significant (over 10-times) mercury retention in fly ash was observed by Wejkowski et al. [52] as a result of the injection of halloysite into the combustion zone of above 850 °C during the combustion of coal in a grate furnace. The metals' sorption ability could provide a solution for the problem of mercury release during the thermal conversion of waste and waste-derived fuels. Mercury is a highly volatile heavy metal whose release occurs even at low conversion temperature [98]. In the flue gas, mercury is present in its elemental form Hg^0, which poses a challenge to common air pollution control devices; thus, adsorption is often considered the most suitable and cost-effective way to remove it from flue gas [99,100]. Several sorbents such as activated carbon or modified fly ashes have been investigated in terms of mercury removal efficiency [101–103], and the presence of alumina and iron was found to promote the adsorption process [104]. These findings, together with the developed specific surface and porosity of aluminosilicates, make them a promising remedy for the Hg^0 problem. The latest research in this field has already appeared, such as work by Duan et al. [105] describing the sorbent based on halloysite nanotubes, which was successfully applied for Hg^0 removal from flue gas.

5. Ash Disposal

The application of aluminosilicates may improve the ash characteristics not only in terms of combustion-related problems but also in terms of possible means of disposal. Ashes from biomass combustion, to meet the requirements of the EU Fertilising Products Regulation 2019/1009 of heavy metals concentration in inorganic macronutrient fertilizers [106], can be utilized for soil conditioning due to their relatively high contents of phosphorous, potassium, and micronutrients [107,108]. The presence of aluminosilicates may enhance the fertilizing properties, as the addition of halloysite was found to improve the urea release of the fertilizer in the study by Wei et al. [109]. In addition, the research of Gilkes and Prakongkep [110] claims that soil kaolin provides an effective substrate for agriculture application in tropical regions.

Some ashes, particularly from waste-derived fuel combustion, may be unattractive for recycling and disposal due to the exceeded leachability thresholds of metals and metalloids. Especially the mobility of lead, cadmium, and zinc, which are highly bioavailable, may be an environmental problem [111]. The addition of aluminosilicates is expected to fix

metals in chemically stable compounds, thus reducing their mobility and leachability. Greinert et al. [112] investigated the ash from the combustion of biomass pellets (80% rye straw, 20% willow wood) with the addition of bentonite in terms of the mobility of heavy metals (Pb, Cd, Zn) and found they were reduced by half by the addition of bentonite during the process of ash granulation. The presence of aluminosilicates may increase the environmental safety of ashes and thus favor their recycling and application according to the principles of the circular economy. Ashes with particularly high concentrations of heavy metals may need immobilization, a process of chemical transformation in such a way that soluble compounds (in this case metals) cannot be eluted. Such ashes can be utilized as components in geopolymers or glass, both of which show very good ability for the immobilization of heavy metals [113,114].

6. Application and Optimal Dosage of Aluminosilicate Clay Minerals

6.1. Determination of the Optimal Additive Dose

The determination of the optimal additive dose and application method was a subject of research, nevertheless, it is still not clearly defined. In general, following the equations presented in Section 3, 1 mol of $Al_2Si_2O_5(OH)_4$ is needed to bond 2 moles of potassium. Hence, the stoichiometric amount of aluminosilicate required can be calculated using the K content of the fuel and the molar weights of the elements. However, the possible impurities must be considered, as industrial-purpose aluminosilicates are not completely pure. Another factor is the occurrence of possible reactions with other ash compounds. The uneven homogenization with fuel or irregular distribution in the volume of the combustion chamber is also relevant, and the local variations in the fuel-additive blends must be also taken into account. Moreover, the process parameters such as the temperature and residence time play a role, and their impact is still under investigation.

Several research papers aim to investigate various doses of aluminosilicates. Wang et al. [115] investigated Danish wheat straw with K content of 16.2 wt.% and Cl content of 3.4 wt.%, and wood pellets with K content of 16.9 wt.% and Cl content of 0.01 wt.%. The combustion of wheat straw took place with the addition of kaolin in a dosage of 3.13% (K/Al ratio 1.0) and 6.2% (K/Al ratio 2.0). In the first case, the deposition tendency of wheat straw decreased from 86% to 29%, and the fraction of potassium bound as a water-insoluble species increased from 36% to 69%. In the case of doubling the kaolin dosage to 6.26%, the water-insoluble potassium compounds in the fly ash increased to 83%. A similar strong increase in bonding potassium to potassium-aluminosilicates was observed for the combustion of wood pellets. On the other hand, in the study by Čepauskienė et al., [116] the incineration of wheat straw was visibly improved with the addition of kaolin at 2% mass ratio, with a slight increase in the amount of ash produced. In the study by Sobieraj et al. [77], the stoichiometric additive (halloysite) ratio was calculated to neutralize the chlorine content in the fuel, taking into account 88 samples of various biomass types. The obtained values are within the range of 0.37–16.19 g halloysite/kg of fuel for wood biomass with Cl concentration of 0.01–0.44 wt.%; 1.10–42.32 g halloysite/kg fuel for herbaceous and agricultural biomass with Cl concentration of 0.03–1.15 wt.%; 0.37–32.02 g halloysite/kg fuel for waste biomass with Cl concentration of 0.01–0.87 wt.%; and 0.37–30.54 g halloysite/kg fuel for contaminated biomass with Cl concentration of 0.01–0.83 wt.%. In general, for most biomasses, the addition of 1–2 wt.% of halloysite was concluded as sufficient to mitigate the unwanted issues.

6.2. Application

When it comes to the application path, the blending of aluminosilicates and biomass during the pelletization process was studied by several researchers. Kuptz et al. [117] investigated the pelletization of biomass with the addition of kaolin. The amount from the stochiometric calculations was raised by 10% to ensure that enough kaolin is incorporated into the pellets. As a result, the additivation level in the range of 0.6–2.3% kaolin on a dry basis was chosen for the biomass composition. It was found that kaolin had only

minor effects on combustion, which was concluded to be due to too low additivation levels. Higher additive mass ratios (up to 15%) were investigated by Li et al. [118] during the combustion of wheat stalk. The prompt potassium retention rate was observed due to the formation of K–Al/Fe silicates, and the trend rapidly increased with the additive ratio (<12%) and only slowly increasing (12–15%).

Admixing aluminosilicates to fuel during the pelletization process is not the only possible application path. Another way is to introduce the additive directly into the combustion zone by an injecting system. This method of application has the advantage of optimization potential in terms of the most suitable temperature zone for the additive injection. Despite the easy optimization potential, the injection of aluminosilicate powders into the combustion zone allows combination with other sorbents, such as urea powder for dry reduction of nitrogen oxides (NO_x) [52] or sodium bicarbonate for dry reduction of sulfur oxides (SO_x) [119,120]. Such technology can be applied in waste-to-energy units, including combustion of medical, industrial, and hazardous waste, where the simultaneous reduction of gaseous pollutants and heavy metals emissions is a key factor of safe operation.

Another advantage of direct injection of additives is adjusting the dosage to the variations in the fuel composition. This is particularly important in the case of MSW and RDF combustion, whose high heterogeneity may result in a local increase in chlorine and alkalis load as chlorine in waste can originate from either organic or inorganic sources. The first group is mainly polyvinyl chloride (PVC), artificial leather, synthetic rubber, and polystyrene foam. The second is kitchen waste contaminated with inorganic chlorides, such as NaCl, KCl, and $MgCl_2$ [121,122]. Similarly, alkali metals can be found in MSW and RDF in a form of inorganic salts, mainly NaCl and KCl, or can be organically associated with materials such as waste wood and leather [123]. In the case of direct injection, the additive dose can be determined on-site based on variations in the waste composition.

When choosing the application path, the temperature and residence time should be taken into account. The influence of temperature, as well as residence time on the performance of kaolin, was investigated by Wang et al. [124]. Kaolin was found to react with KCl and form potassium aluminum silicates despite the temperature. However, at 900 °C, the overall KCl–capturing efficiency of kaolin slightly decreased from 45% to 43% as the residence time increased from 1 h to 12 h. At 1000 °C, the capturing efficiency significantly decreased to 26% (1 h) and 17% (12 h). Such a decrease of the KCl–capturing efficiency was concluded to be a result of the kaolin surface area degradation caused by increasing temperature and heating time. Similarly, Dragutinovic et al. [74] found kaolin successful in preventing ash sintering up to 1100 °C and only partially successful at a higher temperature. The problem of surface area degradation of kaolin was observed as well by Nowak Delgado et al. [125] during the pulverized-fuel combustion of biomass.

7. Limitations

The fact that the application of aluminosilicates as fuel additives leads to increased ash content cannot be dismissed. Nevertheless, according to the reviewed research, doses of 1–5% are usually considered, with a focus on stoichiometric or slightly over stoichiometric values. As a result of additivation, the combustion by-product can be considered as aluminosilicate-modified ashes, featuring enhanced sorption properties [126,127]. Such ash, if it meets the specific criteria (e.g., metals thresholds), may be beneficial not only for sorption but for agricultural or construction applications, as well. According to the principles of the circular economy, aluminosilicates themselves have been proven to positively influence mortar performance [128] and support soil fertility [109,110]. Therefore, further research in this field is required.

Another issue is the proper mixing of an additive with fuel which needs to be secured during the combustion process. Some research indicates that using aluminosilicate powders of fine particle size distribution is required and is especially important for pulverized fuel combustion units [75]. Therefore, the additives may need to be ground before use.

However, the grinding process would be neither difficult nor costly due to the low hardness of aluminosilicates (1–2 on the Mohs scale).

Another challenge may be the proper homogenization of the fuel-additive mix. The aluminosilicate powders are characterized by a high density of about 3 g/cm^3, while some biomass may feature a density of approximately 0.2 g/cm^3. This problem can be solved by using fine-grained aluminosilicates or avoided by their direct injection into the combustion chamber.

Aluminosilicates are raw materials that need to be sourced from underground deposits, which may cause environmental issues and generate operational costs. The current price level of halloysite from a European mine is about USD 200 per tonne, pure kaolin starts from USD 300 per tonne, and bentonite is up to USD 220 per tonne [129]. Bentonite deposits are usually quite large, with lenticular layers only a few meters deep. Nevertheless, because of its hygroscopic nature, its sourcing is a difficult process that must be carried out at a controlled temperature so as not to damage its molecular structure.

8. Conclusions

The interest in the thermal conversion of biomass and waste is expanding; nevertheless, their fuel characteristics are usually not advantageous. Their unfavorable chemical compositions may lead to issues such as the formation of deposits on heating surfaces of a boiler, slagging, fouling, high-temperature corrosion, bed agglomeration in circulating fluidized bed boilers and increased particulate matter emission. With relatively low investment cost and unproblematic management, aluminosilicate clay minerals seem to be a promising solution to these problems. Their application as fuel additives influences the combustion process by changing the ash characteristics. Therefore, the following positive effects can be observed:

(1) The ash fusion temperatures are elevated as a result of bonding potassium into the compounds with melting points of above 1500 °C. This leads directly to the reduction of slagging, fouling, ash deposition, and bed agglomeration in CFB furnaces.
(2) The risk of chlorine-induced corrosion is reduced, as aluminosilicates favor the release of chlorine in the form of hydrogen chloride and thus reduce its presence in ash deposits.
(3) The formation and emission of the particulate matter are minimized, as aluminosilicates reduce the release of ash-forming components into the gas phase.
(4) Heavy metals are expected to get fixed in ash; consequently, their emission into the gas phase is expected to be reduced.

In support of the European Commission's Green Deal concept, the European power sector is aiming to reduce its carbon emissions by 30% by 2030, and aluminosilicate clay minerals used as fuel additives are one of the potential allies in this regard. Their use may increase interest in the thermal conversion of unattractive fuels, such as waste biomass, high-chlorine biomass, RDF, or municipal waste, thus providing a solution to the global energy problem. Clay minerals are an abundant and widely available resource; nevertheless, the fact cannot be dismissed that they are raw materials that are sourced from natural deposits. Companies, entities, or institutions that wish to incorporate aluminosilicate fuel additives must consider their economic and environmental relevance.

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