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Artículo de Revisión

ADDITIVES FOR THE REDUCTION OF ALKALI CHLORIDES DURING BIOMASS COMBUSTION: A REVIEW

ADITIVOS PARA LA REDUCCIÓN DE CLORUROS ALCALINOS DURANTE LA COMBUSTIÓN DE BIOMASA: UNA REVISIÓN

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ABSTRACT

Introduction:
The number of steam generators that burn biomass for steam production is constantly growing. One of the problems they face is severe corrosion, a consequence of the content of alkali chlorides and other corrosive species that these biofuels contain.
Objective:
To carry out a bibliographic review on the use of additives to reduce the effects of the presence of alkali chlorides in biofuels used in steam generators.
Materials and Methods:
References were consulted from 1998 to 2023 related to the main alternatives for the

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mitigation of the effects of corrosion, caused by the presence in biomass (used in combustion for electricity generation) of a high concentration of alkaline chlorides, going deeper into the use of different types of additives or mixtures of them.

Results and Discussion:

Several of the reported methods have medium to high effectiveness in reducing corrosion and the complexity of their implementation. The main additives found are ammonium sulfate, based on aluminum and silicon, calcium and sulfur. The best effectiveness-complexity balance corresponds to the use of kaolin.

Conclusions:

Alkali chlorides increase the corrosion rate of materials used in steam superheaters. Reactions between the metal surface and these species, or others that contain alkalis must be avoided to reduce corrosion in them, for which additives capable of sequestering alkalis from the biomass can be used, forming less aggressive compounds.

Keywords: additives; biomass; chlorides; corrosion; steam generators.

RESUMEN

Introducción:

El número de generadores de vapor que combustionan biomasa para la producción de vapor crece constantemente. Uno de los problemas que enfrentan los mismos es la corrosión severa, consecuencia del contenido de cloruros alcalinos y otras especies corrosivas que estos biocombustibles contienen.

Objetivo:

Realizar revisión bibliográfica sobre el uso de aditivos para disminuir los efectos de la presencia de los cloruros alcalinos en los biocombustibles utilizados en los generadores de vapor.

Materiales y Métodos:

Se consultaron referencias desde el año 1998 hasta el 2023 relacionadas con las principales alternativas para la mitigación de los efectos de la corrosión, provocada por la presencia en la biomasa (utilizada en la combustión para la generación eléctrica) de una elevada concentración de cloruros alcalinos, profundizándose en el uso de diferentes tipos de aditivos o mezclas de ellos.

Resultados y Discusión:

Varios de los métodos reportados tienen una efectividad de media a alta en la reducción de la corrosión y en la complejidad de su implementación. Los principales aditivos encontrados son sulfato de amonio, a base de aluminio y silicio, de calcio y de azufre. El mejor balance efectividad-complejidad corresponde al empleo del caolín.

Conclusiones:

Los cloruros alcalinos aumentan la velocidad de corrosión de los materiales utilizados en los sobrecalentadores de vapor. Las reacciones entre la superficie metálica y estas especies, u otras que contienen álcalis deben evitarse para disminuir la corrosión en ellos, para lo cual se pueden usar aditivos capaces de secuestrar los álcalis de la biomasa, formando compuestos menos agresivos.

Palabras clave: aditivos; biomasa; cloruros; corrosión; generadores de vapor.

1. INTRODUCTION

The negative environmental consequences of the fossil fuels consumption and reserves concern and the supply of fuels have motivated the efficiency optimization in the extraction, transportation, consumption, and conservation of these, and at the same time, the search for resources and renewable energy sources (Badii et al., 2016).

The energy is a central part of the current life and the population uses the resources and energy sources without thinking. The reality is that most of the energy is generated from the fossil fuels burning, such as coal, fuel oil or gas. Currently, these fuels provide 66% of the world electric power, and at the same time, they constitute 95% of the world energy demand, including heating, transportation, electricity generation and other uses. The accumulation of carbon dioxide released by the burning of fossil fuels contributes to global warming and leads to changes in the environment and, consequently, in our social and economic realities.

One of the viable alternatives that has been used with greater emphasis is biomass (Antunes & de Oliveira, 2013), especially that which originates from sugarcane. As the world moves towards replacing fossil fuels, the number of biomass burning steam generators for electricity production is constantly growing. These use various biomass types, such as forest residues, wood and recycled wood, industrial residues such as sugarcane bagasse and sugarcane straw, as well as other residues.

One of the most serious problems faced by biomass combustion plants is severe corrosion, especially at high temperatures, and deposits. Tillman et al. report that the corrosion problems caused by biofuels generally come from the chlorine and alkali metals (mainly potassium and sodium) that they contain (Tillman et al., 2009). Biofuels derived from wood and other crop wastes have higher concentrations of chlorine than coal itself. In steam generators that use biomass, this causes metal degradation, tubes failures and leaks, and shortens their useful life, with economic and safety repercussions (Wang et al., 2012).

Currently, the uncertainty in the availability of sustainability criteria for good quality woody biomass, i.e. with a low ash content, mainly derived from stem wood, added to the growing demand for biomass fuels, has led to the rise of the pellet industry to try to diversify raw material sources. Other types of biomasses such as bark, non-woody biomass (cereals and herbaceous materials), and residues from the agricultural industry, such as sugarcane straw, are also potentially useful as raw materials due to the large volumes available. However, the challenge of these fuels is that their composition varies depending on the type of biomass, which significantly affects their combustion behavior (Míguez et al., 2021).

Mentioned high heterogeneity of biomasses, composition and the variable nature of the aforementioned combustion problems make it difficult to use a "one size fits all" additive, leading to the need for a better understanding of the impact of different additives depending on the biomass composition and combustion conditions (Míguez et al., 2021).

During combustion, a part of the ashes goes to the grate and another part is carried away by the gases. These latter interact directly with the metallic parts (mainly pipes) of the steam generators, reacting directly with the surface oxides and metals, favoring the development of chemical reactions that cause degradation of the latter.

As reported by Nielsen, gas phase corrosion attack can be originated from various chlorine containing species, the most common being hydrogen chloride (HCl) and dichlorine (Cl_2) (Nielsen et al., 2000). The former is the dominant chlorine (Cl) species in most of the gas, but Cl_2 can be present locally at higher temperatures and in the absence of moisture, and can be formed in the reducing environment by thermal decomposition of HCl. This phenomenon is accelerated at high temperatures, which corresponds to high steam parameters. The incidence of corrosion is very marked in steam superheaters that work at high temperatures.

Corrosion in steam generators can be slowed down or even prevented. Several methods have been used for this purpose: the control of excess air, the use of protective coatings based on nickel and iron, the use of refractory coatings and resistant alloys, the pre-treatment of biomass to modify its chemical characteristics and the use of chemical additives. The purpose of this last method is to reduce the catalytic action of SO_2 on hot surfaces, neutralize the acids formed on the surface, prevent the formation of corrosive substances on hot surfaces and reduce the tendency to sinter deposits at high temperatures by raising the melting point of the ashes. Another alternative is to limit the maximum temperatures and steam pressure, although this could reduce the plant's heat and power production capacity, which will reduce its overall efficiency and profitability.

The objective of this review is to carry out a bibliographic review on the use of additives to reduce the effects of the presence of alkali chlorides in biofuels used in steam generators.

2. MATERIALS AND METHODS

The bibliographic references consulted cover the broad period between 1998 and 2023, emphasizing the last decade. Topics related to the use of different types of additives or mixtures of them in biofuels are addressed with the aim of preventing or minimizing the effects of corrosion in the metals of the steam generators, which are essentially due to the high content of alkali chlorides from the biomass used.

For the analysis, several topics were selected such as the specific characteristics of each additive, the effects they have on the corrosion and ash formation processes, the chemical reactions and physical interactions that are verified, the application areas in steam generators, the effectiveness, cost, availability and feasibility of their practical application.

3. RESULTS AND DISCUSSION

3.1. Use of additives in biomass combustion

Fuel additives play an important role in controlling deposits and corrosion (Mangla et al., 2017). They can be added to the fuel in different zones of the boiler: before combustion, directly in the combustion chamber or in the flue gas stream. In all cases, chemical reactions occur to oxidize, neutralize and convert combustion residues that can cause increased corrosion and slagging.

According to Shao et al., the use of additives to solve corrosion problems is based on the idea of transforming the vaporized inorganic species into less volatile forms, increasing the melting temperature of the ashes through chemical reactions and physical interactions; e.g. absorption/dilution and reducing the formation of fine particles or water soluble alkalis (Shao et al., 2012).

Karlsson et al. reported corrosion tests carried out on 304L stainless steel with high chromium content and found that the corrosivity of alkali chlorides is due to the formation of alkali metal chromates, formed by the reaction between the protective oxide and alkali chlorides in the deposit, resulting in a rapidly growing and poorly protective iron-rich oxide (Karlsson et al., 2015). The addition of sewage sludge (a mixture of water and solids resulting from the application of various treatments to wastewater, such as the sediment decanted from the black liquor from the paper mills) to the fuel, which changes the composition of the deposit, and significantly reduces the corrosion rate. The main reason for this could be that the chloride alkalis in the deposit are largely replaced by less corrosive alkalis such as sulfates, alkali phosphates, and aluminum silicate.

During biomass combustion, chlorine-induced corrosion can be reduced by using additives through the following ways (Antunes & de Oliveira, 2013):

a) Prevention of the release of gaseous potassium chloride (KCl).
b) Reaction with KCl forming fewer corrosive species (Broström et al., 2007).

A number of key reactions that could occur between additives and biomass fuels containing alkalis, mainly potassium (K) species, are presented below (Shao et al., 2012):

$$2KCl + SO_2 + ½\, O_2 + H_2O \rightarrow K_2SO_4 + 2HCl \quad (1)$$
$$KCl + SO_2 + O_2 \rightarrow K_2SO_4 + Cl_2 \quad (2)$$
$$Al_2O_3.xSiO_2 + 2KCl + H_2O \rightarrow K_2O.Al_2O_3.xSiO_2 + 2HCl \quad (3)$$
$$2KCl + H_2O + Al_2O_3 \rightarrow 2KAlO_2 + 2HCl \quad (4)$$
$$2KCl + SiO_2 + H_2O \rightarrow K_2O.SiO_2 + 2HCl \quad (5)$$
$$SO_2 + ½\, O_2 \rightarrow SO_3 \quad (6)$$
$$(NH_4)_2SO_4 \rightarrow 2NH_3 + SO_3 + H_2O \quad (7)$$
$$Fe_2(SO_4)_3 \rightarrow 3SO_3 + Fe_2O_3 \quad (8)$$
$$Al_2(SO_4)_3 \rightarrow 3SO_3 + Al_2O_3 \quad (9)$$
$$SO_3 + 2KCl + H_2O \rightarrow 2HCl + K_2SO_4 \quad (10)$$
$$KCl + CaHPO_4.2H_2O \rightarrow CaKPO_4 + 2H_2O + HCl \quad (11)$$
$$K_2O.SiO_2 + 2CaCO_3 \rightarrow 2CaO.K_2O.SiO_2 + 2CO_2 \quad (12)$$

Generally, the additive is required to have a small particle size and a high surface area to facilitate physical adsorption and chemical reactions achieving higher reaction efficiency.

3.2. Main additives currently used

The main characteristics of the best-known additives reported in the reviewed literature are described below.

3.2.1. Ammonium sulfate $(NH_4)_2SO_4$ (ChlorOut process)

The process known as ChlorOut is referred in several publications (Antunes & de Oliveira, 2013; Viklund, 2013; Kassman et al., 2008; Andersson, 2002). It consists of the atomization of an aqueous ammonium sulfate solution in the turbulent zone at the inlet of the steam superheaters with the aim of inducing the sulfation of gaseous alkaline chlorides in the combustion gas.

In this case, the decomposition of the ammonium sulfate into NH_3 and SO_3 occurs first, according to:

$$(NH_4)_2SO_{4(s)} \rightarrow 2NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \quad (13)$$

Subsequently, the sulfation of alkaline chlorides by SO_3 is verified, according to:

$$SO_{3(g)} + H_2O_{(g)} + 2KCl_{(g)} \rightarrow 2HCl_{(g)} + K_2SO_{4(g)} \quad (14)$$

In steam generators using biomass and waste, with steam temperatures range between 400-550 ºC, condensation of alkali chlorides on the surface of the superheater tubes is very likely. The application of $(NH_4)_2SO_4$ reduced the gaseous KCl and also reduced the chlorine content in the deposits significantly better than sulfur (Kassman et al., 2013).

The effectiveness of this method in reducing the rate of corrosion and deposits has been highlighted by (Broström et al., 2007). Henderson and collaborators also confirmed the success of this treatment when firewood is used (Henderson et al., 2006). Viklund et al. demonstrated that ammonium sulfate greatly reduces the amounts of chlorine in the flue gases (Viklund et al., 2009), and Kassman et al. confirm that the use of the mentioned additive reduces the chlorine content in the deposits to negligible amounts during biomass combustion in a large circulating fluidized bed (CFL) boiler (Kassman et al., 2011, Kassman et al., 2013).

It is reported by Broström et al. that pulverized $(NH_4)_2SO_4$ in flue gases reduces the KCl concentration from more than 15 ppm to approx. 2 ppm, and decreases ash deposition rates and corrosion rates, in a 96 MW (thermal)/25 MW (electric) Circulating Fluidized Bed (CFB) boiler burning bark with a chlorine-containing residue (Broström et al., 2007). Kassman et al. confirm the above and propose several strategies that can be applied to reduce operational problems in an LFB boiler (Kassman et al., 2017). These researchers present some operational experience with steam superheater corrosion during the burning of demolition wood. When the pipes were analyzed after two years of operation, it was observed that the corrosion of the steam superheater had a significant reduction with the application of the ChlorOut process. These facts were validated in the longer term in the installations with and without the supply of $(NH_4)_2SO_4$. In addition, $(NH_4)_2SO_4$ has a significant inhibitory effect on the release of nitrogen monoxide (NO), as reported (Wang & Liu, 2020).

Figure 1 shows evidence of the effectiveness in reducing corrosion with the use of the ChlorOut process in a corrosion probe exposed during four weeks at different conditions (Kassman & Berg, 2006).

Normal fuel mix   Normal fuel mix + ChlorOut

Figure 1. Effectiveness of the ChlorOut process

Source: (Kassman & Berg, 2006)

In this way, it is possible to implement the ChlorOut process in a boiler that operates regularly, taking into account that the most important thing is the installation of a $(NH_4)_2SO_4$ injection system, with continuous control of the alkalis, through the IACM. According to Kassman et al., (2017), $(NH_4)_2SO_4$ is supplied in the form of a 40% mass aqueous solution. In another application in a non-lignocellulosic waste incinerator (Kassman et al., 2017), Viklund et al. injected 0.5 L of the solution per hour of work in a 75 MW boiler, in a ratio equivalent to 60 kg of sulfur/h (Viklund et al., 2009). While Broström et al. used this system for a 97 MWt boiler fed with wood pellets (62 L/h ratio of solution with an injection system similar to the one installed by (Kassman et al., 2017) and determined the ratio of 100 g of S/MWh (Broström et al., 2007).

3.2.2. Kaolin or kaolinite

Several researchers have reported the use of kaolin or kaolinite ($Al_2Si_2O_5(OH)_4$) as an additive in biomass combustion (Aho and Silvennoinen, 2004; Öhman et al., 2004 and Wei et al., 2005). Steenari et al. suggest that in this case the kaolin aluminosilicates join the potassium according to the following possible reactions (Steenari et al., 2009):

$$Al_2Si_2O_5(OH)_4 + 2KCl \rightarrow 2KAlSiO_4 + H_2O + 2HCl \quad (15)$$

$$Al_2Si_2O_5(OH)_4 + 2KCl + 2SiO_2 \rightarrow 2KAlSi_2O_6 + H_2O + 2HCl \quad (16)$$

$$Al_2Si_2O_5(OH)_4 + K_2SO_4 \rightarrow 2KAlSiO_4 + 2H_2O + SO_3 \quad (17)$$

$$Al_2Si_2O_5(OH)_4 + K_2SO_4 + 2SiO_2 \rightarrow 2KAlSi_2O_6 + 2H_2O + SO_3 \quad (18)$$

Pure kalsilite ($KAlSiO_4$) and leucite ($KAlSi_2O_6$) have high melting points of 1600 °C and 1500 °C, respectively, resulting in fewer corrosion problems compared to KCl and K_2SO_4 with low melting points and which can form deposits on the surface of the steam superheater (Theis et al., 2006). According to Steenari and Lindqvist another advantage of kaolinite is that it reduces sintering problems by increasing the melting point of the ash (Steenari & Lindqvist, 1998).

Keizer reported that Al-Si based additives such as kaolin (40:60 wt% $Al_2O_3.SiO_2$ hydrate) react with chloralkalis to form alkali aluminum silicates found in coarse fly ash particles (Keiser, 2013).

For an LFC boiler, from a 12 MW plant (Pettersson et al., 2009), the use of kaolin is reported, together with the commercial zeolite (Doucil 24A) ($(Na_2O)(Al_2O_3)(SiO_2)_2$ 2.8 H_2O), in a flow of 40 kg/h; which would result in an expense of 3.33 kg/MWh. The additives were added directly to the fluidized bed of the boiler. The composition of the kaolin used was 46.6% SiO_2 and 39.5% Al_2O_3, while for the industrial zeolite (Doucil 24A) it was 39-43% SiO_2, 33.5-36.5% Al_2O_3, 0.0032% FeO and 23.5-25.5% Na_2O, with a density of 400-600 g/dm^3 and particle size between 1 to 5 µm, dosed with fuel in a molar ratio 1:1.

According to Davidsson et al., kaolin is used in steam generators in the form of a fine powder (< 2 µm) and is placed in the bed in direct contact with the gas flow (Davidsson et al., 2007). On average, a kaolin dose of 0.15% (on a dry basis) can be used with respect to the mass of the fuel, although in the case of agro-industrial residuals its use has been reported between 0.25 and 0.8 times the initial biomass (Aho, 2001). To determine the exact dose to be used, it must be taken into account that a 1:1 molar relationship should be started between the content of alkali in the fuel and the aluminum (Al) in the kaolin and, on the other hand, high levels of calcium (Ca) in the fuel reduce the efficiency of the process, so the percentage of kaolin should be increased. According to Brunner et al. the properties of the kaolin, such as particle size and moisture, also significantly influence the efficiency of the alkali reduction process (Brunner et al., 2019).

The application of additives based on Al-Si, especially kaolin, has been adopted with optimism due to its availability; however, its price continues increasing, which threatens its continued use by the biomass conversion industry. Sewage sludge, that is, alum sludge, is a cheap, easily available and proven alternative to combat the deposition of ash in biomass, which is why these industries should adopt its use to avoid the danger that looms with the increase in the cost of kaolin (Abioye et al., 2023).

3.2.3. Halloysite

Mroczek et al. made a valuable contribution by finding a solution to the kaolinite problem and replacing kaolinite with halloysite ($Al_4(OH)_8Si_4O_{10}.10H_2O$), an aluminosilicate clay mineral (Mroczek et al., 2011). The advantage of using it instead of kaolinite is related with the structure of halloysite. This is represented in Figure 2 and, as can be seen, it is formed by silicon tetrahedrons and aluminum octahedrons, forming a single plate that is separated from the next one by a space in which the K^+ can be inserted. The high reactivity of halloysite can be explained by the presence of two hydroxyl groups (OH^-): one located internally between the tetrahedral and octahedral layers and a superficial one located in the octahedral layer. Such an arrangement gives rise to an interesting bonding structure in which bonds between ions can occur both in the surface layers and in the interior of the crystal.

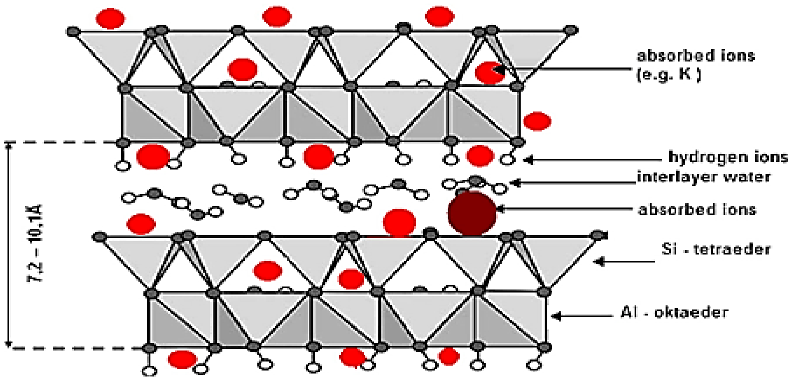

Figure 2. Structure of the halloysite with possible location of absorbed ions.
Source: (Mroczek et al., 2011)

Mroczek et al. demonstrated that proper mixing of halloysite with biomass can reduce corrosion at high temperatures during combustion, effectively lowering chloride-alkali concentrations in ash deposits. The authors fixed a fraction of halloysite in relation to the mass of the sample in the range of 1-2% by weight and carried out tests under real conditions, confirming the suitability of halloysite as an additive for biomass combustion processes.

For the addition of halloysite to the steam generator, they recommended the following variants:

1. During the preparation of fuels, for example, during the manufacture of briquettes or pellets from biomass.
2. In the form of a fine powder in the biomass feeding system.

Other authors reported the use of halloysite in boilers in amounts between 1-4% by mass and supplied it in powder form with a particle size between 0.04-0.15 mm. They also refer to the use of a homogeneous mixture with the initial biomass (Mroczek et al., 2011).

3.2.4. Other aluminum-silicon based additives

The use of aluminum-silicon based additives has the main objective of increasing the melting temperatures of alkaline compounds in the combustion or co-combustion of biomass. A large number of reports appear in the literature due to their high capacity to convert the compounds KCl and K_2SiO_3 in the vapor/liquid phase into potassium and aluminum silicates, such as $KAlSiO_4$, $KAlSi_2O_6$, $KAlSi_3O_8$, etc., with high melting temperatures (>1100°C) (Pettersson et al., 2009; Steenari et al., 2009).

Other aluminum and silicon-based additives that have been reported are: acid activated bentonite (Aho, 2001), bauxite (Shao et al., 2012) and glass powder (Aho, 2001). In the latter case, it is supplied before the biomass enters the steam generator.

In all cases, it is suggested that to improve the effectiveness of the additive it is required that it should be in the form of small particles for a greater surface area, facilitating physical adsorption and chemical reaction.

3.2.5. Sulfur based additives

These are also additives used to increase the melting points of alkaline compounds in the combustion or co-combustion of biomass. A certain number of sulfur (S) in the combustion gases can facilitate the sulfation of alkali chlorides and make the ashes less sticky, as well as increase the melting point of the deposits. Karlsson et al. reported that the use of sulfur-containing additives or by co-combustion with a sulfur-rich fuel mitigates the corrosive environment in a boiler (Karlsson et al., 2015). This is due to the conversion of corrosive alkali chlorides into less corrosive alkali compounds, such as, alkali sulfates. The non-corrosive behavior of alkaline sulfates has been explained by other authors as their inability to react with chromium-rich oxide to form alkaline chromates.

The substances used in this type of additives can be: granulated elemental sulfur or also ammonium, iron or aluminum sulfates. The ChlorOut variant, previously analyzed, is very effective for the application of sulfur-based additives.

Another widely used and reported alternative is the use of SO_2, which converts NaCl and KCl into sulfates, which are much less corrosive than chlorides. When this method is used, the steam temperature can be higher than 400 °C, but at temperatures higher than 550 °C the sulfates formed also cause corrosion problems. The SO_2 is obtained from the system itself, by installing a device for the in-situ separation of SO_2 from the gas flow in an ash treatment module, which then recirculates the captured SO_2 to the boiler inlet (Hunsinger & Andersson, 2014). Using the recirculation system there is an increase of 500 mg/N.m^3 of SO_2.

It has been reported by Keizer that co-firing of corrosive biomass fuels, with high sulfur fuels, not only dilutes the corrosive fuel but also converts the salts that would form chloride-alkali fuel ash deposits into sulfates alkaline (Keiser, 2013). With the addition of sulfur to the biomass fuel, Johansson changed the fly ash particles mainly from KCl to K_2SO_4. K_2SO_4 deposits are much less corrosive than KCl, mainly due to their higher melting temperature: 1069 °C compared to KCl's 770 °C (Johansson et al., 2008).

3.2.6. Calcium-based additives

Calcium (Ca)-based additives such as lime and limestone may be effective by diluting the ash or adsorbing alkaline salts on their porous surfaces when calcined rather than chemically reacting with alkali metals or compounds containing alkalis. The calcination process usually occurs at high temperatures and long time. However, calcium additives containing CaO, $CaCO_3$ and $Ca(OH)_2$ are more active in biomass combustion to help convert potassium species in the steam to high melting potassium silicates/phosphates (Shao et al., 2012). These substances are known as: lime or quicklime (CaO), calcite ($CaCO_3$), and dead lime or hydrated lime ($Ca(OH)_2$).

The raw material for lime is limestone rock (calcareous rock or simply limestone), which has a high calcite ($CaCO_3$) content. The calcite ($CaCO_3$) from the limestone rock is transformed by heat into lime (CaO) and by adding water it becomes slaked lime ($Ca(OH)_2$).

According to Wang and Liu, the joint use of co-firing and chemical additives is suitable for CFB bed boilers (Wang & Liu, 2020). The chemical additives used in co-combustion to reduce the calcium-based chlorine content are: CaO, $CaCO_3$ and $Ca(OH)_2$. According to the research of (Zhu et al., 2008) the inhibitory effect of $Ca(OH)_2$ and CaO is stronger than that of $CaCO_3$.

In the case of limestone, Öhman et al. proposed to mix the additive with the biomass prior to combustion by preparing the mixture through a sludge (particle size between 1-2 μm) that allows the additive-fuel mixture to be homogenized in such a way that it represents an additive-dry/fuel ratio of 0.5% on a dry basis (Öhman et al., 2004).

3.2.7. Other additives

Li et al. used a horizontal tube furnace to study the inhibitory effect of various additives on the corrosion of the metal heating surface of biomass-fired boilers. A significant decrease in the corrosion rate of the metal samples is observed through the addition of kaolin, pulverized coal ash, silica fume, dolomite, limestone and bauxite. When kaolin, pulverized coal ash, silica fume, and bauxite are used as additives, corrosion is almost completely inhibited. By using dolomite and limestone, the inhibitory effect is poor, although the corrosion rate is also reduced. The corrosion ability of alkali metal chloride is higher than that of alkali metal sulfate. Different additives have different inhibitory effects on them (Li et al., 2020).

Additionally, Steenari and Lindqvist suggested that minerals such as kaolin and dolomite have been used as fuel additives to give the ash a higher melting point. High-temperature reactions between straw ash and kaolin, ($Al_2Si_2O_5(OH)_4$), or dolomite, ($CaMg(CO_3)_2$), respectively, were therefore investigated. Kaolin was found to be the more effective additive. The reaction between kaolin and potassium salts in straw ash gave $KAlSiO_4$ and $KAlSi_2O_6$. A laboratory study of reactions involving K_2SO_4 or KCl and kaolin showed that several products are possible, one of which is $KAlSiO_4$. The potassium capture by kaolin partly explains the higher melting point of the ash-additive mixture. Dolomite added to wheat and barley ash reacted with silica to form silicates. No reaction between dolomite and potassium compounds was observed. The observed enhancement of the melting point caused by dolomite is probably an effect of dilution or adsorption (Steenari & Lindqvist, 1998).

3.3. Comparative analysis of additives

Table 1 presents a comparative summary between the different additives discussed in this article, taking into account the effectiveness in reducing corrosive processes of the metal parts of the steam generator, the complexity of the additive injection system, its relative cost in the international market and whether its industrial use in sugarcane agricultural residues (RAC) has been reported. From the given information, it is possible to evaluate the best feasibility of each additive.

Table 1. Comparison of different additives. Source: (Rubio-González et al., 2021)

Additive	*Effectiveness in reducing corrosion*	*Complexity of the supply system*	*Relative cost (national production)*
Ammonium sulphate	High	Low	Very low (No)
Kaolin or kaolinite	Medium	Low	Low (Yes)
Halloysite (clay)	High	Low	High (No)
Granulated elemental sulfur	High	High	Low (Yes)
Quicklime	Medium	Low	Low (Yes)
Calcite (limestone rock)	Medium	Low	Medium (Yes)
Hydrated lime	Medium	Low	Low (Yes)

From the analysis of the types of chemical additives evaluated in this section, it is inferred that several of the methods have a medium to high effectiveness in reducing corrosion, and in terms of the complexity of their implementation. There are two methods that require the installation of pressure injection systems at various points in the boiler and a rigorous control system in terms of injection moment and time, as well as injection parameters such as droplet size and cone penetration. Although it is not shown in Table 1, the use of SO_2 seems to be the most complex of all the additives due to the continuous SO_2 separation system in the flow that must be implemented.

Those that involve initial mixing in a certain proportion between biomass and additive should be assessed for implementation, as they are the alternatives with fewer technological complications and in some cases with comparatively low costs.

The best balances between effectiveness-complexity-relative costs correspond to the use of limestone or kaolin, as well as ammonium sulfate. The logistics and supply chain of these additives must be assessed for their application in order to implement this method in the generation of electricity from the combustion of biomass under the conditions of each country.

4. CONCLUSIONS

1. Alkali chlorides, especially potassium chloride, increase the rate of corrosion of materials used as steam superheater tubes. Reactions between the metal surface and this species, or other alkali-containing species, such as carbonates, should be

avoided to reduce corrosion in steam superheaters.

2. Corrosion mitigation methods are designed to prevent the metal surface from reacting with aggressive alkali-containing species. This can be achieved through different alternatives, including the use of additives that contain sulfur or other species capable of sequestering alkali from the biomass, forming less aggressive compounds such as alkaline sulfates of aluminosilicates, instead of alkaline chlorides.

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CONFLICTS OF INTERES

The authors declare that there are no conflicts of interest.

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