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(54) **ADDITIF DESTINE A ETRE INJECTE DANS DES CHAMBRES DE COMBUSTION D'INSTALLATIONS DE CHAUFFE, ET PROCEDE POUR EMPECHER LA CORROSION A HAUTE TEMPERATURE**

(54) **ADDITIVE TO BE SPRAYED INTO THE COMBUSTION CHAMBERS OF HEATING PLANTS AND PROCESS FOR PREVENTING HIGH TEMPERATURE CORROSION**

(57) L'invention concerne un additif destiné à être injecté dans des chambres de combustion d'installations de chauffe et d'incinération de déchets pour empêcher la corrosion à haute température et réduire la proportion de cendres volantes dans les gaz de combustion. L'invention concerne également un procédé pour empêcher la corrosion à haute température et réduire la proportion de cendres volantes dans les gaz de combustion produits dans des chambres de combustion d'installations de chauffe et d'incinération de déchets. L'additif est constitué de bentonite activée par voie acide et/ou de matières fondues d'oxydes, notamment de verre pulvérisé ou de poussière de verre présentant un point de fusion inférieur à 1000 °C. Ledit additif est injecté dans la chambre des gaz, dans des zones où la température des gaz est supérieure à 700 °C.

(57) An additive is sprayed into the combustion chambers of heating and waste incineration plants to prevent high temperature corrosion and to reduce the fly ash proportion in the exhaust gas. Also disclosed is a process for preventing high temperature corrosion and for reducing the fly ash proportion in the exhaust gas from heating and waste incineration plants. The disclosed additive consists of acid activated bentonite and/or oxide melts, in particular glass powder or glass dust with a melting point below 1000 °C, and is sprayed into the gas chamber in areas in which the gas temperature exceeds 700 °C.

Abstract:

Additive for Nozzling into Combustion Chambers of Firing Means
and Method for Preventing High Temperature Corrosion

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The invention relates to an additive intended to be nozzled into combustion chambers of firing means and waste incineration plants for preventing high temperature corrosion and reducing the portion of flue dust contained in the combustion offgases as well as a method for preventing high temperature corrosion and reducing the flue dust portion contained in the combustion offgases of firing means and refuse incineration plants. The additive is comprised of acidically activated bentonite and/or oxide melts, in particular glass powder or glass dust having a melting point of below 1000°C, and is nozzled into the gas space in zones exhibiting gas temperatures of above 700°C.

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Method for Preventing High Temperature Corrosion

The invention relates to a method for preventing high temperature chlorine corrosion in combustion chambers of firing means and waste incineration plants and reducing the flue dust portion contained in the combustion offgases.

Known methods for preventing corrosion were aimed at reducing corrosion in incineration plants and, in particular, on the heat exchanger surfaces of boilers by effecting reactions in the gas phase in order to deactivate corrosive substances. To this end, magnesium oxide is usually nozzled in, thereby enabling primarily high temperature sulfate corrosion to be substantially reduced at temperatures of above 480°C. This is obtained in that, at an excess of MgO contained in the deposits forming, for instance, on the superheater tubes, MgSO₄ instead of alkali pyrosulfates is formed with the SO₂ of the smoke gas. At temperatures of above 480°C alkali pyrosulfates will, in fact, dissolve the layer of scale, thus leading to catastrophic corrosion damages.

MgO is ineffective against corrosive damages caused by chlorine forming during the sulfation of chlorides.

That type of corrosion has been increasingly encountered in the firing space regions of refuse incineration plants during the past years, since the composition of refuse has changed on account of refuse separation, on the one hand and a higher smoke gas temperature must be observed as in accordance with legal provisions, on the other hand (800°C for at least 2 seconds within the combustion chamber).

From WO 95/11287 it has already become known to nozzle cerium compounds such as iron cerium, cerium oxides and/or cerium oxide hydrates in powder form. According to that previous proposal, it was possible to nozzle in such cerium compounds together with magnesium oxide, primarily aiming at

- 2 -

substantially reducing the cleaning expenditures involved in the removal of deposits from the internal sides of plant parts and thereby enabling longer campaign times than in known processes. In particular, it was intended to preserve the action of, and no longer deteriorate, passivating layers already formed on the upper surfaces of plant parts for the protection of the same. Those cerium compounds such as iron cerium, cerium oxide or cerium oxide hydrate were to safeguard reducing zones in the vicinity of the walls in order to thereby reduce corrosion. The effect of cerium compounds in the manner of oxidation catalysts induces afterburning in reducing regions of the smoke gas, thereby reliably preventing the reduction of an oxide layer of scale or rust already formed for passivation. The cerium compounds also were to become active against chloride ion corrosion in order to thereby ensure oxidation to basically less dangerous chlorine gas in molecular form.

The use of additives of this type, however, involves relatively high costs and has proved to be insufficiently effective, in particular in connection with high temperature chlorine corrosion, in which chlorine gases dissociate again.

Attempts to admix to the charging material to be burnt filtering aids and, in particular, inorganic filtering aids based on active silicic acid containing silanol groups likewise have proved to be relatively expensive, since additives will show effects only in percentage ranges due to their being inhomogenously distributed in refuse.

For recycling into the circuit of a melting chamber firing means pollutant-loaded residues such as, for instance, filter ashes, adsorbents or the like while adding used glass and/or limestone chips, DE-A-4 021 362 has already proposed to introduce the absorber into the circuit of a melting chamber firing means with complete ash recycling. The absorber may be fed into the the smoke gas path and/or into the ash

- 3 -

recirculation and/or into the slag discharge and/or along with coal, wherein broken used glass and/or limestone chips may be dosed in.

5 From GB-A-1 307 127, the use of 85 % by weight of calcium bentonite, 10 % by weight of sodium phosphate and 5 % by weight of sodium borate in oil, gas and coal firings may be taken for granted. US-A-3 249 047 proposes the introduction of
10 antimony compounds and silicates having large specific surfaces in the overheating zone of coal-fired boilers in order to reduce SO₃ corrosion.

Finally, GB-A-800 445 suggests to use burnt bentonite and other refractory materials in order to enhance the
15 distribution of oil droplets in gas turbines.

The invention aims at providing a method of the initially defined kind, in which even the slightest amounts of an additive may be employed with alkali and the content of metal
20 chlorides in the smoke gas being reducible as quickly as possible. The reaction is to start as rapidly as possible and to occur even at high temperatures without releasing elementary chlorine.

25 To solve this object, the method according to the invention for reducing high temperature chlorine corrosion in firing means and incineration plants, wherein additives are nozzled into the gas space, essentially consists in that acidically activated bentonite is nozzled into the gas space at gas
30 temperatures of above 750°C, preferably 800°C. Due to the high reactivity of acidically activated bentonite it is even feasible already at relatively high temperatures to effect the desired reaction for binding alkalis, the desired reactions proceeding rapidly and quantitatively even at temperatures of
35 above 900°C. Very quick alkali binding, therefore, is achieved if the additive is nozzled in along with secondary air closely above the burner plane or the grate, for instance in the plane

of the secondary air supply, so as to be able to substantially reduce the distance over which a corrosive attack may happen at all. In order to enhance the distribution of the acidically activated bentonite, the latter optionally may be nozzled in
5 together with silicon dioxide, SiO_2 becoming active primarily as a diluent. In any event, acidically activated bentonite in mixtures with SiO_2 is to be used in amounts of more than 50 % by weight, based on the mixture, in order to rapidly ensure the desired reaction.

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By nozzling in glass dust it can be ensured that the glass dust or glass powder will rapidly melt completely, wherein an effective protection of the boiler walls to be protected against corrosion may be enhanced in that the glass dust or
15 glass powder is introduced in the direction of the walls of the gas space via directed nozzles or spraying discs. In this manner, a rinsing flow of glass melt is safeguarded along the walls of the gas space.

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In accordance with the invention, glass dust or glass powder advantageously is nozzled into the gas space in amounts of from 0.3 kg/ton to 30 kg/ton refuse, wherein ground used glass such as, e.g., window glass or bottle glass may simply be used. Advantageously, glass ground to grain sizes of about 50
25 μm is used for the method according to the invention.

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Advantageously, it is proceeded in a manner that acidically activated bentonite optionally mixed with SiO_2 is nozzled into refuse incineration plants in amounts of from 0.5 to 3.0
kg/ton refuse.

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A particularly economic process control enabling further reduction of pollutant emissions may be achieved in that acidically activated bentonite is used for adsorbing harmful
substances such as Hg or dioxin in the cooled offgases of incineration plants, in particular in a flue flow process, and subsequently is nozzled into the combustion chamber.

Due to the conditions prevailing within the firing chamber, alkaline chloride is formed in quite considerable amounts at the high chlorine contents usually present in refuse these
5 days. The ratio between chlorine and sulfur with refuse in smoke gas has shifted in favor of chlorine during the past years, elevated amounts of metal chlorides getting into the smoke gas undecomposed and being converted into sulfates only there or in the deposits. Under the given thermodynamic
10 conditions such a reaction, which is also called sulfation reaction, results in sodium sulfate and elementary chlorine and hence in a strong corrosive attack. The chlorine even reaches the tube surface and there can destroy steel while forming iron chloride. Such a sulfation reaction in the firing
15 chamber mainly is to be observed behind and closely above the brickwork, and the nozzling in of acidically activated bentonite according to the invention renders feasible an extremely rapid reduction of the metal chloride content. Proposals to nozzle sulfur into the smoke gas for that purpose
20 bring about an acceleration of chloride sulfation, yet sulfation will occur only at lower temperatures and the amount of released chlorine will be the same. Acidically activated bentonite, due to its chemical and physical properties, is able to react with alkaline compounds in the smoke gas
25 extremely rapidly even at elevated temperatures, in particular at temperatures of above 900°C, wherein alkali can be bound and HCl is formed. Thus, no elementary chlorine is released and the risk of high temperature chlorine corrosion is substantially lowered.

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According to the invention, a cost-effective and simple additive to be additionally used for nozzling into the combustion chambers of firing means and refuse incineration plants, which enables boiler campaigns to be substantially
35 increased and which, at the same time, aims to drastically reduce the portion of flue dust contained in the offgas, which is still relatively high in case of known additives, was

obtained from oxide melts, in particular glass powder or glass dust having a melting point of below 1000°C. Glass powder or glass dust, which preferably is nozzled in in counterflow to the smoke gases, melts at the temperatures prevailing in the combustion chambers, binding flue dust to water insoluble glasses. At the same time, surprisingly also alkali is rapidly bound into such melting glass powder or glass dust particles with a rapid reduction of the chlorine content in the offgases likewise having been observed in a surprising manner. All of these corrosive components of the combustion offgases are, thus, effectively bound by the melting glass powder or glass dust particles with the additional advantage being obtained of the melt forming a dense deposit on the boiler walls, which will prevent corrosive attacks, flowing down along the walls in the direction towards the slag as a liquid melt film. Such a rinse of the boiler walls by the molten glass melt in addition to a corrosion-reducing effect on the boiler walls to be protected, thus, also has the advantage of a number of noxious substances being effectively dischargeable by the downwardly flowing melt. Such an additional additive may be nozzled in along with acidically activated bentonite, thereby enhancing the effects to go even beyond the sum of the individual effects.

Advantageously, glass powder or glass dust having a melting point of below 800°C is used, complete melting and the safe delivery of the noxious matter dissolved in the melt being ensured in that the glass powder or glass dust has a mean grain size of 30 to 60 μm , preferably 40 μm .

In the following, the invention will be explained in more detail by way of two diagrams. In Fig.1 of the drawing the amount of sodium chloride as well as the SO_2 equilibrium partial pressure are plotted over the temperature for the firing chamber conditions indicated below. $p_{\text{CO}_2} = 0.2$ bar, $p_{\text{H}_2\text{O}} = 0.2$ bar, $p_{\text{O}_2} = 0.05$ bar, $p_{\text{HCl}} = 10^{-5}$ bar and $p_{\text{Cl}} = 10^{-5}$ bar. From that illustration according to Fig. 1 it is apparent

- 7 -

that the formation of sodium chloride in the firing chamber occurs primarily in the high temperature range and it is, therefore, aimed at eliminating sodium chloride from the smoke gas already at high temperatures.

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In Fig. 2 the amount of sodium chloride in mg/m^3 is plotted over the temperature. Curve 1 indicates the reduction to be attained by nozzling in 1 kg of acidically activated bentonite per ton of refuse. Curve 2 shows the effect that would be achievable by nozzling in 2 kg of sulfur, this clearly illustrating the superiority of nozzling in acidically activated bentonite for the purpose of lowering the sodium chloride portion at high temperatures. On the other hand, Curve 3 clearly shows the effect if only 1 kg of sulfur is nozzled in and Curve 4 indicates the effect with pure smoke gas.

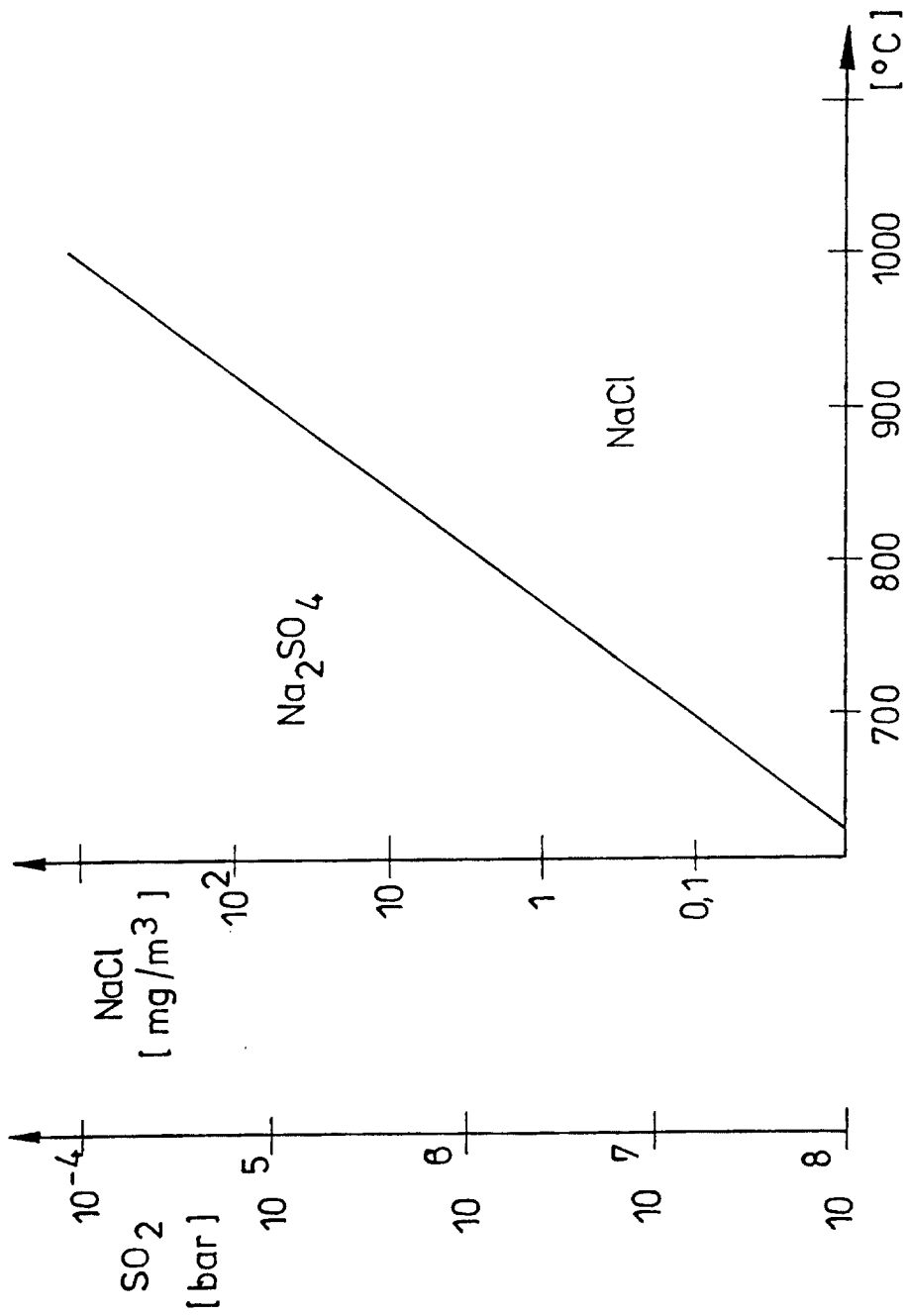
The additive is in powder form and may readily be prepared in a grinding fineness that allows the additive to be nozzled directly into the firing chamber via secondary air.

When simultaneously nozzling in glass, corrosion-resistant linings of the boilers were formed and the pollutant emission was lowered, the service life of the means following upon the firing chamber, such as superheaters or the like, having been improved as well.

Claims:

1. A method for preventing high temperature corrosion and reducing the portion of flue dust contained in the combustion offgases of firing means and waste incineration plants, characterized in that acidically activated bentonite is nozzled into the gas space at gas temperatures of above 750°C, preferably 800°C.
2. A method according to claim 1, characterized in that acidically activated bentonite in mixtures with SiO₂ is nozzled in, the portion of acidically activated bentonite being larger than 50 % by weight, based on the mixture.
3. A method according to claim 1 or 2, characterized in that acidically activated bentonite optionally mixed with SiO₂ is nozzled into refuse incineration plants in amounts of from 0.5 to 3.0 kg/ton refuse.
4. A method according to any one of claims 1, 2 or 3, characterized in that ground used glass such as, e.g., window glass or bottle glass is used as SiO₂ component.
5. A method according to any one of claims 1 to 4, characterized in that acidically activated bentonite is used for adsorbing harmful substances such as Hg or dioxin in the cooled offgases of incineration plants, in particular in a flue flow process, and subsequently is nozzled into the combustion chamber.

FIG.1



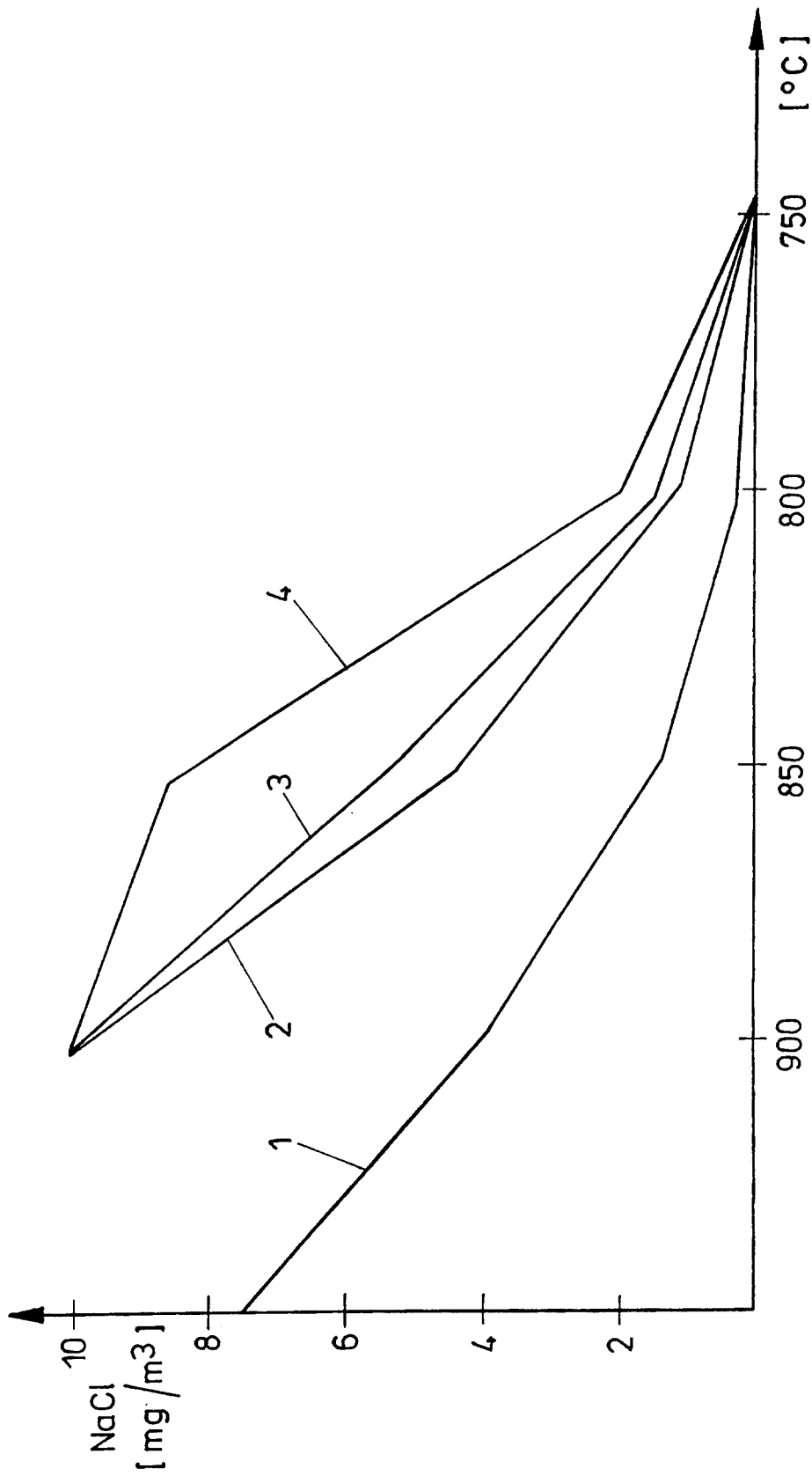


FIG. 2