(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 058 086 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 82300638.2

(22) Date of filing: 09.02.82

(51) Int. Cl.³: C 10 L 10/00
C 10 B 43/00

(30) Priority: 09.02.81 GB 8103859

(43) Date of publication of application: 18.08.82 Bulletin 82/33

(84) Designated Contracting States: AT BE CH DE FR IT LI LU NL SE

(71) Applicant: POLARCHEM LIMITED
Lee House London Wall
London EC2(GB)

(72) Inventor: Walden, Ulf Thore
25 Boulevard du Larvotto
Monte-Carlo(MC)

(72) Inventor: Weigand, Erich
2105 Seevetal 3
Am Fuchshang(DE)

(74) Representative: Allard, Susan Joyce et al,
BOULT, WADE & TENNANT 27 Furnival street
London EC4A 1PQ(GB)

(54) Method for the prevention of deposits on or the removal of deposits from heating and ancillary surfaces.

(57) A method for preventing deposits on or removing deposits from heating and ancillary surfaces of boilers and like equipment, which method comprises continuously or intermittently introducing into the combustion chamber of the equipment or into the flue gas stream in atomized form by means of at least one injection device a liquid additive comprising an aqueous solution of a mixture of ammonium nitrate, at least one nitrate of an alkali metal, optionally at least one nitrate of an alkaline earth metal and an indicator, monitoring the pH value or the additive and, if necessary adjusting the pH value to within the range of from 7 to 9, monitoring the dewpoint of the flue gas stream and adjusting as necessary, the amount and composition of the additive supplied to the metering device in order to adjust the dew point of the flue gas stream to the desired level.

EP 0 058 086 A2

0058086

METHOD FOR THE PREVENTION OF DEPOSITS ON OR THE REMOVAL OF DEPOSITS FROM HEATING AND ANCILLARY SURFACES

The present invention relates to a method for the prevention or removal of soot and other deposits from heating and ancillary surfaces, which deposits are formed as a result of the combustion of gaseous, liquid and solid fuels, and also to the reduction of corrosion of these surfaces by the lowering of the acid dewpoint of the combustion gases. In particular the invention relates to the removal of deposits from and the prevention of corrosion of heating and ancillary surfaces such as boiler and economiser tubes, in turbo-compressors, turbo-chargers, exhaust-boilers, gas turbines, process furnaces and other equipment.

By the term "deposits" as used herein is meant the deposits formed from the products resulting from the combustion of gaseous, liquid and solid fuels. The deposits may consist of carbon, in the form of soot, or may comprise sulphur and/or sulphur compounds or the ash of fuels, which are generally argillaceous compounds when the fuel is coal or a product thereof, and vanadium compounds when the fuel is an oil.

The deposits are generally hard and adherent. When deposits are formed on steel or other metals, then because the thermal conductivity of the deposits is low compared with that of the steel or other metal, the rate of heat transmission from the flame or hot gases to the water or other fluid which is being heated is reduced, thereby reducing the efficiency of the equipment.

The deposits may also increase the corrosion of metal surfaces by trapping corrosive agents, such as acid sulphates, therein. At high temperatures, in the absence of liquid water, these sulphur compounds do not normally cause corrosion and it is usual to maintain the combustion gases at a temperature above that temperature (the "dew point") at which liquid can form. However, when there is a deposit on a metal surface the temperature at the metal surface itself may be below the "dew point" whilst the temperature of the gases is above the "dew point". The deposit thus increases the risk of corrosion.

The present invention provides a method for preventing deposits on or removing deposits from heating and ancillary surfaces of boilers and like equipment, which method comprises continuously or intermittently introducing into the combustion chamber of the equipment or into the flue gas stream in atomized form by means of at least one injection device a liquid additive comprising an aqueous solution of a mixture of ammonium nitrate, at least one nitrate of an alkali metal, optionally at least one nitrate of an alkaline earth metal and an indicator, monitoring the pH value of the additive and, if necessary adjusting the pH value to within the range of from 7 to 9, monitoring the dewpoint of the flue gas stream and adjusting as necessary, the amount and composition of the additive supplied to the metering device in order to adjust the dew point of the flue gas stream to the desired level .

The additive which is used in the present invention may be composed as follows:

Ammonium nitrate	up to 40% by weight
Alkali metal nitrate	up to 50% by weight
Alkaline earth metal nitrate	0 to 80% by weight
Water	up to 75% by weight.

The preferred alkali metal nitrate for use in the additive is potassium nitrate and the preferred alkaline earth metal nitrate is magnesium nitrate.

The indicator may be any suitable indicator which will indicate the pH of the additive, thereby indicating whether or not the pH is within the range of from 7 to 9. The pH of the additive is preferably in the range of from 8 to 9 and thymol blue or bromothymol blue may be used to give an indication of a pH within this range. The pH may be adjusted as necessary by the addition of a base, e.g. potassium hydroxide.

The dewpoint of the flue gas may be monitored by any conventional dewpoint meter.

The reactions will occur in the neutralization of gases containing sulfur oxides are as follows:-

$Mg(NO_3)_2 \cdot 6H_2O = MgO + NO + NO_2 + O_2 + 6H_2O$.

100 $Mg(NO_3)_2$ gives 16g MgO

$MgO + SO_3 = MgSO_4$

$\therefore$ 16 g MgO neutralizes 32gSO_3

$2KNO_3 = K_2O + NO + NO_2 + O_2$

100g KNO_3 gives 47g K_2O

$K_2O + SO_3 = K_2SO_4$

$\therefore$ 47g K_2O neutralizes 40g SO_3

In addition, the nitrogen oxides produced as a result of the decomposition of the nitrates affect the reactions occurring. The nitrogen oxides thus react with the sulphur oxides to form the anhydride of nitrosylsulphuric acid. This is a stable compound excluding water or up to a sulphuric acid concentration of 80%. Even at a 70% sulphuric acid concentration (corresponding to a flue gas temperature of about 100°C) decomposition is slight. The compound leaves the combustion chamber undecomposed and does not cause any corrosion.

During the operation of the method of the invention the additive is fed into the combustion chamber or flue gas stream, the composition of the additive and the volume thereof being adjusted to suit the plant being treated and the problems associated with the particular fuel being burnt. The additive is effective both at high temperatures, i.e. $>1000^{\circ}C$, and at low temperatures, i.e. $>100^{\circ}C$.

In a preferred mode of operating the present invention aqueous solutions of the nitrates are provided in separate tanks. The required amounts of each of these ingredients is then supplied in the desired amount to a common tank for mixing prior to introduction into the combustion chamber or flue gas.

In operating the method of the invention a reduction in the temperature of the flue gases usually occurs and this leads to a reduction in flue-gas heat loss with a concurrent fuel saving.

The present invention will be further described with reference to the following Examples.

EXAMPLE 1

A STEINMULLER water-tube boiler was treated with the aim of decreasing the heating-surface contamination and thus keeping the flue-gas temperature almost constant during a 3-month seasonal operation.

Steam output	30 t/hour
Steam pressure	40 bar
Steam temperature	475°C
Fuel	fuel oil S
Fuel throughput	60 t/day

2 steam-pressure burners.

Composition of the additive

Potassium nitrate	15%
Ammonium nitrate	10%
Demineralised water	75%
Indicator	thymol blue traces

Addition: O2 litres of the additive per ton of fuel

Injection point: combustion chamber 1 injection lance

Injection appliance: fully automatic, time-controlled pneumatic operation

Results

The heating an ancillary surfaces were free of solid deposits, and the surfaces could be dry cleaned using compressed air.

The flue-gas temperature rise during the operation was only 6°C as compared with 35°C according to the previous operating records.

A reduction in flue-gas heat loss of 2%, was achieved which was equivalent to a fuel saving of about the same order.

EXAMPLE 2

A MAN water-tube boiler was treated with the aim of keeping the heating and ancillary surface deposit rate as low as possible over a 12 month period and of reducing the dew point from 134°C to about 105°C.

Steam output:	25 t/hour
Steam pressure	60 bar
Steam temperature	510°C
Fuel	fuel oil S
Fuel throughput	50 t/day

2 steam-pressure burners.

Composition of the additive:

Magnesium nitrate	30%
Potassium nitrate	10%
Ammonium nitrate	6%
Demineralised water	54%
Indicator	thymol blue traces

Addition: continuous, i.e. 0.4 litres of the additive per ton of fuel oil.

Injection point: combustion chamber 1 injection lance

Injection appliance: semi-automatic; pump operation

Results: The heating and ancillary surfaces were up to 85% free of solid deposits. The surfaces could be dry cleaned by means of compressed air and no wet cleaning was required in the combustion chamber.

The acid dew point was reduced to 102°C accordingly, the steam-operated air-preheater could be used without fear of corrosion.

The flue-gas temperature of initially 172°C adjusted itself to 145°C; i.e. the flue-gas heat loss was reduced by about 1.5%, equivalent to a fuel saving of about the same order and, additionally, a steam saving in the air-preheater, so that an improvement in efficiency of about 2.5% overall was achieved.

EXAMPLE 3

A VKW- Lentjes Benson boiler was treated.

Steam output	90 t/hour
Steam pressure	120 bar
Steam temperature	520°C
Fuel	Heavy fuel oil - sulphur content 1.25% by weight maximum
Fuel throughout	6 t/hour
6 burners	
Fuel oil temperature	132°C

0058086

Composition of the Additive	per litre
Magnesium nitrate	700 g
Potassium nitrate	50 g
Ammonium nitrate	33 g
Demineralized water	507 g
Indicator bromothymol blue	traces
pH value 7-8 Colour:	blue specific gravity ca 1.29

Flue gas parameters	
Flue gas volumes	70,000 NM^3/L
Flue gas temperature	165°C
CO_2 content	14.5% max 15.4%
O_2 content	0.25%
SO_3 content	17 mg/Nm^3 = 5 ppm
SO_2-SO_3 conversion	0.84%
Acid dew point	123°C

Addition

Addition of the additive took place continuously at a rate of 4.9 litre by means of injection lances securely installed in the combustion chamber. Pump units fed the additive from the storage containers to the injection lancers. It was thus possible to match the output of the pump units to the desired reduction in acid dew point.

Results

The additive was used over a relatively long period of time. The acid dew point was lowered to 60-62°C and the flue gas temperature was set at 147°C. It was possible to blow or dust off the residues on the heating and ancillary surfaces with compressed air when the boiler was taken out of operation. The lowering of the sulphuric acid dew point by about 60°C enabled an economy to be made in the steam required for the air preheater, without any fear of corrosion.

CLAIMS

1. A method for preventing deposits on or removing deposits from heating and ancillary surfaces of boilers and like equipment, which method comprises continuously or intermittently introducing into the combustion chamber of the equipment or into the flue gas stream in atomized form by means of at least one injection device a liquid additive comprising an aqueous solution of a mixture of ammonium nitrate, at least one nitrate of an alkali metal, optionally at least one nitrate of an alkaline earth metal and an indicator, monitoring the pH value of the additive and, if necessary adjusting the pH value to within the range of from 7 to 9, monitoring the dewpoint of the flue gas stream and adjusting as necessary, the amount and composition of the additive supplied to the metering device in order to adjust the dew point of the flue gas stream to the desired level.

2. A method as claimed in claim 1 wherein the alkali metal nitrate is potassium nitrate.

3. A method as claimed in claim 1 or claim 2 wherein the alkaline earth metal nitrate is magnesium nitrate.

4. A method as claimed in any one of the preceding claims wherein the indicator is thymol blue or bromothymol blue.

0058086

5. A method as claimed in any one of the preceding claims wherein the pH value of the additive is adjusted to within the range of from 7 to 9 by the addition of an alkali.

6. A method as claimed in any one of the preceding claims wherein the injection device is an injection lance.

7. A method as claimed in any one of the preceding claims wherein aqueous solutions of the nitrates are provided in separate tanks.

8. A method as claimed in claim 7 wherein the aqueous solutions of the nitrates are supplied in the desired amounts to a common tank for mixing prior to their introduction into the combustion chamber or flue gas.

SJA/pd/EA 535