Review

Reliability of Flue Gas Desulphurisation Installations - the Essential Condition of Efficient Air Pollution Control

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Abstract

In order to minimise the adverse effects of SO_2 and SO_3 on the environment, many power plants and industrial facilities use flue gas desulphurisation (FGD) scrubbers to remove SO_2 and SO_3 from combustion gases. The conditions within a scrubber and accompanying installations are very severe and cause corrosion problems for common engineering materials. Failures impend over the environment for lengthy periods. This paper describes recent experience with corrosion and new construction materials of full-scale wet FGD systems. Materials description includes advantages and disadvantages, application areas, testing methods and relative costs of various materials.

Keywords: air pollution control, flue gas desulphurisation (FGD), material evaluation, corrosion

Introduction

Combustion of conventional fuels such as hard coal and brown coal, oil and natural gas cause pollution of the atmosphere with sulphur oxides (SO_2 and SO_3), nitrogen oxides (NO_X) and dust [1-3]. Discontinuing use of these energy sources in the nearest future seems unlikely [4, 5]. Hence, the only acceptable solution is application of appropriate technologies and equipment eliminating substances hazardous for the environment formed from fuels or after combustion of waste gases [6-8]. Unfortunately, it was found that environmental conditions inside these types of installations are corrosively very severe, that traditional construction materials in these installations undergo rapid destruction, causing breakdowns, ineffective desulphurisation, pollution of the atmosphere and high economic losses [9, 10]. In general, it also undermined the conviction about possibilities of effective flue gas desulphurisation (FGD), this being a very disadvantageous situation. Production of materials assigned especially for application in FGD installations was the solution. Awareness of existence of these types of material and the need for their application in FGD installations seems to be insufficient.

The aim of this paper is to review new materials and modern protection technologies of traditional materials used in FGD installations warranting long operation of installations. Their properties are described, areas of application in FGD installations, selection methods, and mutual cost relations. Knowledge of possibilities of modern materials application in installations for protection of air will lead to an increase in the

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reliability of FGD installations and a decrease of operating costs.

Methods of Fuel or Flue Gas Purification

Burning of different types of coal causes largest emission of SO_2 and SO_3. The contents of sulphur in coal are in the 0.2-11% range. Usually, it is found in the form of pyrite (FeS_2), (30-70% of the total quantity of sulphur). Other inorganic and organic compounds make up the remaining part. Sulphur and sulphur compounds can be removed from coal at different stages [11]:

- preparation of coal for combustion,
- during combustion,
- after combustion, from waste gases.

Coal desulphurisation before combustion is economically uncompetitive in relation to other methods, hence is applied in a limited scale. Pyrite (FeS_2) is removed by physical and chemical methods. The density of pyrite (5 g/cm^3) is over two times greater than that of other minerals (1.8-2.2 g/cm^3). This fact is used in the physical method. The flotation process is used for separation of fine particles. Sulphur in the form of organic compounds is removed by chemical methods. In general, these methods are expensive and complicated, they cause large losses of coal and therefore are rarely used in practice. Removal of sulphur from crude oil is applied much more frequently. In this case the contents are lower and usually are found in the range from 0.1 to 3%.

Desulphurisation during burning is realised in the industrial scale in fluidised beds. During combustion injection proceeds of ground limestone or dolomite or the combustion process proceeds in a fluidised bed with the addition of limestone or dolomite. SO_2 formed during combustion of coal reacts with these substances becoming part of ash. A low degree of utilisation of limestone or dolomite and a low desulphurisation efficiency prevented the method from finding application in large energy-producing units.

A decrease in the emission of sulphur compounds to the atmosphere in the industrial scale is obtained most frequently by desulphurisation of waste gases. The first FGD installations in power plants were constructed in the seventies in Japan and USA, and in the eighties in Europe. Approximately 90% of all FGD installations use the wet lime/limestone method [12]. According to [8] the share of this desulphurisation method is equal to 83% in USA, 56% in Japan and 93% in Germany. In industrial conditions, especially in electric power plants, it is the only practically applied desulphurisation method. Other methods are applied on a small scale, in the case of small quantities of flue gas and small flow rates; they are characterised by lower desulphurisation effectiveness and higher costs. The wet lime/limestone method is characterised by high desulphurisation effectiveness reaching 93-97%, it can be applied in the presence of large volumes of flue gas streams, changing parameters and flue gas composition and is relatively inexpensive. Apart from these basic advantages, it also has drawbacks. Due to the aggressive chemical environment (condensing sulphuric, hydrochloric or possibly nitric acid, presence of dust containing chlorides, sulphates and fluorides), elevated temperatures and danger of erosion inside the installation, it is necessary to use durable construction materials or special anticorrosion linings protecting traditional construction materials. Dry and semi-dry methods are used in a limited scale, mainly in small installations. This situation results from the fact that wet methods allow a degree of flue gas desulphurisation required by government regulations, usually 92-97%, while dry and semi-dry methods are characterised by a relatively low flue gas desulphurisation degree, usually 40-60%.

Corrosion Hazard

An FGD installation working by the wet method is made up of areas of differentiated hazard. In Fig. 1. a schematic diagram has been presented of an FGD installation working by the wet lime/limestone method. Hazards exist inside the installation, which can be divided into the corrosion, temperature and erosion types [13] (Table 1). The greatest corrosion problems are observed in the vicinity of the scrubber, the purified gas zone and the chimney. The temperature of flue gases obtained from the boiler usually reaches 160 to 180°C. In these conditions the hazard is relatively low, as condensation of acids does not occur. If the flue gas temperature does not decrease, due to application of thermal insulation of walls, then in the area of the entrance of flue gases to the scrubber (or pre-scrubber, depending on the construction) the application of ordinary carbon steel is possible.

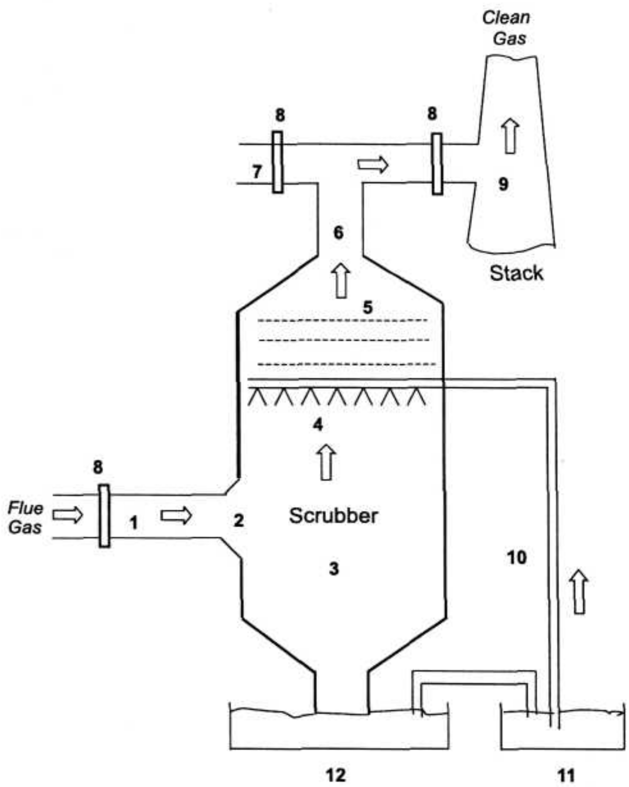

Fig. 1. Schematic diagram of a wet lime/limestone FGD system. Numbers refer to Table 1.

Table 1. FGD system components and environmental hazards inside installation.

	Component	Corrosion	Erosion	Thermal effects
1	Inlet duct	1	1	2
2	Scrubber inlet	3	2	2
3	Scrubber body	3	3	2
4	Slurry nozzles	2	3	2
5	Mist eliminator	3	2	2
6	Scrubber outlet	3	2	2
7	Bypass duct or reheaters	3	2	3
8	Dampers	3	2	3
9	Stack breeching	3	2	3
10	Slurry piping	3	2	2
11	Alkali tanks	1	2	1
12	Recycle tanks	3	2	2

Notes: 3 – severe problem, 2 – minor problem, 1 – not usually a problem.

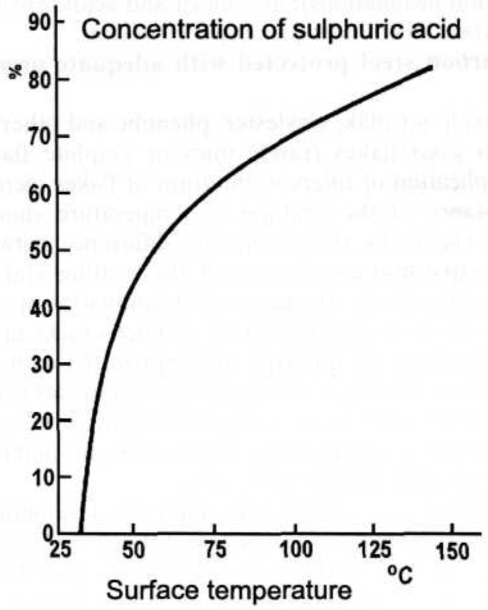

Fig. 2. Concentration of sulphuric acid in the condensate vs. the wall temperature at an 8% water vapour content [15].

The situation drastically changes when the flue gas temperature decreases below the so-called acidic dew-point of the respective acid, at which condensation on the installation walls occurs [14]. First, concentrated sulphuric acid condenses, at lower temperatres hydrochloric and nitric acid. The temperature at which this occurs depends on the partial pressure of SO_3 and water vapour. In typical combustion conditions this temperature is in the 120 to 150°C range. The concentration of sulphuric acid in the condensate depends on the concentration of water vapour and SO_3 in the flue gas and the wall temperature. Fig. 2 presents the relation of the concentration of sulphuric acid from the wall temperature at an 8% water vapour content [15]. It can be easily seen that the wall material, during temperature changes, should be resistant in a wide range of sulphuric acid concentrations. In order to avoid corrosion problems it is essential to apply appropriate thermal insulation of ducts to the scrubber so that the flue gas temperature does not decrease below the dew-point of sulphuric acid. It is not possible in the scrubber which due to the presence of a lime or limestone suspension flue gas has to be cooled first. This is performed in a prescrubber and also in a heat exchanger heating the purified gas flowing to the chimney. In the scrubber sulphur dioxide is chemically captured by lime or limestone slurry by the following fundamental reaction:

$$\text{Lime: } Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O \quad (1)$$

$$\text{Limestone: } CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \quad (2)$$

The resulting product, calcium sulphite, is oxidised to calcium sulphate by oxygen present in the flue gas:

$$O_2 + 2CaSO_3 \rightarrow 2CaSO_4 \quad (3)$$

The scrubber is endangered by interaction of an acidic condensate containing chlorides and fluorides at a temperature of 40-80°C and erosive interaction of dust. Similar conditions are found in the purified gas zone, where there is also a hazard connected with condensation of sulphuric acid, as purified gases contain some quantity of unremoved SO_3, or in some FGD units its content increases as a result of mixing with unpurified flue gas. The aim of such proceedings is to increase the purified gas temperature and avoid sulphuric and hydrochloric acid condensation in the chimney. The same aim is met by heating purified gases in a heat exchanger before forwarding them to the chimney.

In [16] the corrosion rate has been presented of ordinary construction carbon steel in flue gas condensation conditions depending on the steel temperature, in industrial conditions in flue gas ducts in a power plant and in laboratory conditions simulating flue gas condensation conditions. The corrosion rate in these conditions is equal to 1 to 7 mm/year. This is an unacceptable corrosion rate in industrial units - causing perforation of the installation usually after one year.

In FGD installations working by the dry method, due to a high process temperature above acidic dew-point temperatures, specially aggressive corrosion conditions are not formed, therefore not justifying the need for application of special materials.

Materials Used in FGD Units

In particular areas the following groups of materials are applied:

a) carbon steel - applied in dry and hot environments (> 150°C) (ducts for unpurified flue gases) and in a basic environment (suspension tanks and suspension preparation installations); in a moist and acidic environment carbon steel undergoes rapid corrosion,

b) carbon steel protected with adequate organic linings:

- epoxide novolak, vinylester, phenolic and other lin ings with glass flakes (rarely mica or graphite flakes) - the application of fillers in the form of flakes increase the resistance of the coatings to temperature changes (thermal shock) by decreasing the difference between thermal expansion coefficients of the coating and the steel base. This limits the danger of delamination of coat ing from the base and formation of microcracks in the coating. Coatings of this type are approx. 0.5 to 6 mm thick and are durable to temperatures of 170-180°C (ep oxide to 110°C). Organic linings are relatively inexpen sive in comparison with other protection means and their durability is estimated at 5-15 years,
- rubber linings - dimensions of flue gas desulphurisation installations make vulcanisation difficult in the tradi tional way. Hence, mixtures of chloroprene and chlorobutyl rubbers are used, which are self-vulcanising at am bient temperatures and atmospheric pressure. Crosslinking of such rubbers begins from the moment of produc tion and therefore their storage in a cold store is required if not used quickly or when the temperature exceeds 25°C. Usually, self-vulcanising linings can be put into op eration after approx. 8 weeks of seasoning at 25°C or after 1-2 weeks at higher temperatures obtained, for example, by treating with hot air. Rubber linings vulcan ised by the manufacturer are more and more frequently used. They can be stored for a longer time on rollers and used shortly after application. At present linings vulcan ised by the manufacturer are most frequently used in FGD installations. In FGD units rubber linings are used for protecting scrubbers, lime suspension sprinkler sys tems, purified gas ducts, pipelines supplying the suspen sion and carrying off gypsum, suspension tanks and water tanks. The following types of rubbers are used: butyl, bromobutyl and chloropren. Rubber layers of 3 to 8 mm thickness are applied. The durability of protection with the use of rubber linings in most aggressive conditions of flue gas desulphurisation installations is estimated at 5-15 years. The advantages of rubber linings in power plants are relatively low protection cost comparable to costs of application of organic linings, and a much lower cost in comparison with high alloy steels, nickel or tita nium alloys. Rubber linings, show high resistance to ab rasion. One of the flaws is the limited temperature resis tance of rubber linings (they can be used up to 70-80°C). Another disadvantage characteristic for rubber linings is difficulty in application (sticking) on more complicated surfaces in shape.

c) carbon steel protected with inorganic linings - in some areas of FGD units (prescrubber, chimney parts) endangered by strong erosive interaction acid resistant brick furnace linings are used. Also, for protection of purified gas zones and chimneys special light bricks made from borosilicate foam glass are used mounted on steel with bituminous-polyurethane mastic. They are characterised by high thermoinsulation and chemical resistance. In general, this type of protection is more expensive than organic protection.

d) stainless steels, nickel and titanium alloys are most frequently used in the form of wallpaper. Steel sheets 1.5 mm thick made of stainless steel, nickel and titanium alloys are welded in a special way to the basic structure made of ordinary construction steel. The following nickel alloys are used: C-22, C-276, C-4, 904L, 31, 59 and others. They are characterised by low carbon content: < 0.04-0.07%, high nickel content Ni : 14-66%, Cr: 16-27% and Mo: 2.6-6.2% and N: < 0.2%. The addition of Mo, N and other components increases resistance of alloys to pitting in an acidic medium with chlorides. Among stainless steels 254 SMO and 654 SMO are used, while G-2 and G-7 among titanium alloys. Metal linings are endangered during operation by pitting, crevice corrosion, galvanic corrosion and corrosion cracking. Mainly, they are used for protection of: scrubbers, prescrubbers, chimneys, heat exchangers, small installation elements (hatches, gate valves, etc.).

A disadvantage of this type of protection is its high cost: greater by several to over ten times the case of organic protection.

Choice of Anticorrosion Protection

Progress in the production of new materials made possible the attainment of long-term durability of a structure operated in most aggressive conditions found in flue gas desulphurisation units. Taking into account the high diversity of fossil fuels, their chemical composition and the installation construction, variable conditions and chemical, temperature and erosion hazards, it is vital to correctly design the anticorrosion protection installation. Protection of chimneys operating with FGD installations is becoming a significant problem [17, 18].

New methods should be used for evaluation and choice of materials, as corrosion tests used until now are not effective due to the extremely high resistance of these materials [19]. Hence, modern testing techniques are used, especially electrochemical techniques: cyclic voltammetry, noise analysis and impedance spectroscopy [20-24]. Elaborated evaluation procedures and measurement methods enable correct choice of protection for most aggressive corrosion conditions occurring in FGD installations.

Conclusions

1. Very aggressive corrosion conditions are encoun tered inside flue gas desulphurisation units working by wet methods, characterised by chemical, temperature and erosion hazards.
2. Application of traditional engineering materials in FGD installations is improper due to their low durability.
3. Special materials exist for use in FGD installations such as:
   - stainless steels and alloys containing significant quantities of chromium, nickel or titanium,
   - composite coatings containing fillers in the form of flakes,
   - special butyl, bromobutyl and chloropren rubbers.

4. In particular areas of FGD installations differentiated corrosion hazards exist, hence application of different types of protection is advisable.

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