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Modern desulfurization methods used in waste incineration equipment

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Abstract

Decreasing the amount of sulfur dioxide emissions is one of the most critical concerns of environmental protection. These substances have huge influence on natural environment as well as on human health. The authors included information about the absorbtion process that takes place in absorbers. Also, the various types of absorbers are presented, along with applications and a short description. There are presented installations placed in Polish waste incineration plants.

Keywords: desulfurization, scrubbers, absorption

Streszczenie

Nowoczesne metody odsiarczania stosowane w urządzeniach termicznej utylizacji odpadów

Zmniejszenie emisji dwutlenku siarki jest obecnie jednym z najważniejszych zagadnień ochrony środowiska. Związki te mają istotny wpływ na środowisko naturalne, w tym zdrowie człowieka. W artykule przedstawiono suche i mokre metody odsiarczania, wraz z ich porównaniem. Zawarto również informacje na temat procesu absorpcji zachodzącego w absorberach. Przedstawiono rodzaje absorberów, ich zastosowanie oraz sposób ich doboru, a także instalacje znajdujące się w polskich spalarniach odpadów.

Słowa kluczowe: odsiarczanie, absorbery, absorpcja

1. Introduction

Air pollution is defined in varied way. It's characterized by the concentration of the harmful substances, and can be presented as the ratio of deleterious substance expressed in milligrams or micrograms in reference to 1 dm^3 of air volume[1].

Air pollution affects not only the environment, but, most importantly, human health. People who live in dense urbanized areas of well developed industry sector are the most vulnerable to harmful substances. Despite the continuous efforts leading to improve the air quality in Poland and Silesia, still there are some periodically occurring issues, connected with high concentrations of many harmful substances. Tropospheric ozone's concentrations become higher during summer. It is formed during reactions of emissions from motor vehicles and nitrogen oxides, in the presence of ultraviolet radiation. Such situation is highly unfavorable, since ozone is a strong oxidizer. Regular exposure to direct contact with this substance can lead to chronic inflammation of respiratory mucus and conjunctiva. Also, it can exacerbate asthma [2]. During winter PM10, PM5 and smaller particles as well as benzopyrene are the most troublesome. These substances are produced by construction materials industry, energy industry and fuels combustion [1]. Particulate matter, when inhaled, can cause irritation of the mucous membranes. The most harmful particles are those smaller than 5 μm, Since they easily penetrate the body to cause upper respiratory tract inflammations, silicosis, lung cancer, allergies and asthma.

Pollution sources can be divided into two groups: natural sources, that are not caused by human activity, such as volcano eruptions or forest fires. The second group are sources influenced by human activity, called anthropogenic pollution sources. Industrial facilities, heat and electricity production facilities, motor vehicles and agricultural facilities are examples of such sources. Liquid and gaseous fuels can be desulfurized before combustion, therefore coal combustion is the main source of sulfur dioxide.

Sulfur dioxide is produced in industrial processes, such as coal, petroleum combustion or waste incineration processes. Liquefied SO_2 is used in refrigeration, paper, paint, textile and chemical industries. When combined with water, sulfur dioxide can cause acid rains (pH lower than 5.65), which can damage plants (especially confiners) and acidify soil, what results in decrease of amount nutrients. Also, acidified soil dissolves lime and cement in buildings. In concentrations even as small as 3 ppm SO_2 irritates respiratory tract and mucus. In higher concentrations and after longer exposure it can lead to life-threatening complications [1].

2. Desulfurization

Many processes can be used to maintain the not life-threatening pollution level. The emissions in flue gases can be reduced after combustion, and the products of such reactions can be then used in production processes. Nowadays one of the most important issues of environment protection is to decrease the emission of sulfur compounds to atmosphere. Sulfur can be removed during preparation of coal to combustion, during the combustion process, or from combustion gases. In commercial scale, liquid and gaseous fuels are defulzurizated before the combustion process. Coal desulfurization in uneconomical comparing to other methods. Desulfurization of combustion gases is the most widely spread [3].

Main principle of desulfurization is transformation of sulfur dioxide in a material, easily removed from combustion gases and from the cleaning system. We distinguish waste and regenerative methods. Disadvantage of waste methods is transportation of pollutions to liquid, solid or both, which deepen the existing problems with waste. In regenerative methods SO_2 reacts with absorbent, which is then regenerated and comes back to the absorption process. However this methods are more expensive. Both waste and regenerative methods can be proceeded as wet or dry. This definition can refer both to final product and application of liquid [3].

2.1. Wet methods

In this article there will be presented two kinds wet method: with application of lime or limestone solution and sodium carbonate.

2.1.1. Lime method

This method is non-regenarative process from the point of view of sulfur recovery and reaction solution. This method is based on absorption and chemical reaction of SO_2 in lime or limestone solution. Forming $CaSO_3$ and $CaSO_4$ as a result of the reaction in form of sludge or moist solid body in most examples are wastes. During absorption of SO_2 in water suspension in the first stage following processes are proceeded [3]:

$SO_{2(g)} \rightarrow SO_{2(aq)}$

$SO_{2(aq)} + H_2O \rightarrow H_2SO_3 \rightarrow H^+ + HSO_3^-$

$HSO_3^- \rightarrow H^+ + SO_3^{2-}$

Solubility of SO_2 in water if function of temperature and decreases with its increase. In practice the liquid is not a pure water, but a solution containing dissolved salts, mainly chlorides, as a result absorption speed is increasing. In case of lime present in absorption process, following reactions are proceeded [3]:

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

$Ca^{2+} + HSO_3^- + 2H_2O \rightarrow CaSO_3 \cdot 2H_2O + H^+$

$2H^+ + OH^- \rightarrow 2H_2O$

In presence of oxygen sulfite ion can oxidize according to following reactions:

$SO_3^{2-} + \frac{1}{2} O_2 \rightarrow SO_4^{2-}$

$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$

According to above reaction we obtain gypsum. Conditions of the process should be matched in the way, so the $CaSO_4/CaSO_3$ ratio was as large as possible, which guarantee good quality of the gypsum. Efficiency of desulfurization depends of stoichiometry ratio of $Ca(OH)_2$ or CaCO according to removed sulfur. Efficiency ηSO_2 = 90% is obtained for ratio 1,05-1,2 for $Ca(OH)_2$ and 1,25-1,6 for $CaCO_3$ [3].

2.1.2. Sodium carbonate method

Blocking, erosion, corrosion of interior of scrubber and accompanied devices were the reason to develop this method, in which solutions of Na_2CO_3 or NaOH are used. During the SO_2 absorption process in scrubber in alkaline solution there is no precipitation of solid. Main stages of the process are [3]:

- SO_2 absorption – removed from dust and wet gases in absorber are in contact with recycled alkaline solution. Following reactions are present in this process in case of using Na_2CO_3:
  $Na_2CO_3+SO_2 \rightarrow Na_2SO_3+CO_2$
  $Na_2SO_3 + SO_2 + H_2O \leftrightarrow 2NaHSO_3$
  $2\ Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$.
- Regeneration – solution from absorption process is in reaction with $Ca(OH)_2$ suspension before going to decanter. Separated crystals of solid in form of sludge is directed to storage area or further processing. Clear liquid is transported to softening process. In regeneration process following reactions proceeds:
  $Ca(OH)_2 + 2NaHSO_3 \rightarrow Na_2SO_3 + CaSO_3 \cdot H_2O\downarrow + H_2O$
  $Ca(OH)_2 + Na_2SO_3 + ½\ H_2O \rightarrow 2NaOH + CaSO_3 \cdot H_2O\downarrow$
  $Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow 2NaOH + CaSO_4 \cdot H_2O\downarrow$
  as a result $CaSO_3/CaSO_4$ mixture is precipitated. This mixture has good filtrating properties.
- Softening – losses of sodium is replenished with soda and there is precipitation of excess calcium ions. Regenerated absorbent goes back to the scrubber [3].

Effectiveness of SO_2 absorption process is limited by speed of SO_2 transporting to the solution and balance in gas-liquid reaction system.

Efficiency of desulfurization is stable and can be maintained above 90-95% with adequate conditions of the process. Absorption can be proceeded in Venturi scrubbers. With good dust extraction from gases, this method can be linked with gypsum production. Operating costs of this method is comparable with $CaO/CaCO_3$ method or even smaller [4].

2.2. Dry methods

In dry methods processes of bounding chemical SO_2 proceeds in dry state, that is, in gas-solid system or desulfurization useful or waste products are forming in dry state. A lot of problems are avoided, such as: precipitation of solids in devices, pH control, heating clean gases and accumulation of liquid wastes. Dry methods are based on adsorption on solid sorbents (metal oxides or active carbon) and absorption with chemical reaction with simultaneous drying of desulfurization products. Dry methods include following processes: direct injection of sorbent into combustion chamber, mixing sorbent with fuel before feeding the boiler [5].

The most widespread dry method is Furnace Sorbent Injection (FSI). It is based on sorbent injection into combustion chamber in optimal temperatures zone, that allows fast desulfurization. Grinded limestone, calcium oxide, hydrated lime or dolomite can be used as sorbet [5].

Reactions proceeded in boiler zone [5]:
$CaCO_3 \rightarrow CaO+CO_2$
$CaO+SO_2 \rightarrow CaSO_3$
$CaSO_3+ ½\ O2 \rightarrow CaSO_4$
$CaO + SO_2 + ½\ O_2 \rightarrow CaSO_4$

There is also possibility of using milk of lime $Ca(OH)_2$ into the combustion chamber [5]:
$Ca(OH)_2 \rightarrow CaO+H_2O$
$CaO+SO_2 \rightarrow CaSO_3$

Decomposition on limestone proceeds in temperature 825˚C – 950˚C. Below lower limit the decomposition not very effective, above the upper limit there is agglomeration of grains and lack of decomposition. Because of weak mixing of sorbent's grains with gases and low reaction speed, effectiveness of dry method is 20% - 40 % and strongly depends on used sorbent excess [5].

2.3. Semi-dry methods

Heat of flue gases are used, in this method, for evaporation of some part of dissolvent, in which the reagent is, that is water. Reaction products are solids and are precipitated from flue gases stream in filtrating device, often bag filter. Also active carbon can be added, which improve the efficiency of the process. Exemplary process consists of:

- flue gases cooling by water injection,
- introduction of reagent (CaO) do the reaction chamber with cooling water, where will be mixed with flue gases and as a result neutralization of acid gases reactions will take place (absorption),

- possible injection of active carbon, which allows adsorption of gaseous pollutions on its surface,
- flue gases purifying in bag filters [6].

Semi-dry method can be also used by injection of milk of lime, which is CaO water solution or suspension. Such solution can cause operating difficulties connected with clogging of atomizers. Injection of dissolved reagent allows to increase their amount by recirculation and dissolution of non-reacted reagent.

The advantages of this methods are: lack of sewers, which need purifying, low water consumption and better energy effects of the installation, because of no heat losses resulting from application of large amount of water, like in wet methods.[6]

2.4. Comparison of wet and dry methods

Comparison of wet and dry methods can refer to reagents and energy requirement, waste accumulation and neutralization, exploitation and economics of the process.

Dry methods with the same efficiency η_{SO2} require slightly bigger stoichiometry ratio of sorbent to SO_2. Sorbents used in dry methods costs more, but use of water is about 50% less or water is not used at all. In most desulfurization processes costs of reagents are evaluated at 25-35% of exploitation costs. This costs can be decreased, if there are possibilities of utilization of alkaline liquid wastes (e.g. in metal, textile or paper industry).
Energy demand in dry methods in lower, because of eliminating operations with huge amounts of suspensions flux and heating dry gases [3].

In lime method above operations use 60-75% of all supplied energy. In dry methods there is better utilization of existing means of transport and there is less problems with accumulation of wastes. Desulfurization products are practically insoluble and easy to convert to granulated products with various application. In dry method there is elimination of devices necessary in wet methods, blocking the interior of devices with deposits and also limitation of corrosion, amount of devices in installation is smaller, which facilitate exploitation with decreased service. This lowers exploitation and investment costs [3].

3. Installations in waste incineration plants

Well designed technological process should be efficient and the emissions of pollutions should be minimized. In waste incineration plant in Dąbrowa Górnicza, in the desulfurization process, there is used scrubber with milk of lime solution which is additionally intensively aerated. As the result of chemical reaction sulfur oxides transforms to gypsum [7].

In Jedlicze, in incineration plant of industrial and medial wastes, there is used high-efficient wet lime method with bag filters. Wastes forming as a result of thermal utilization are gathered in concrete boxes [8]. At the turn of 2013/2012 there will be built new waste incineration plant in Kraków, where municipal wastes will be utilized. Flue-gases purifying system will be semi-dry. In the system there will be no waste products and there will be used agents based on limestone and active carbon [9].

In newly forming waste incineration plant in Ruda Śląska and Łódź there will be used semi-dry method with application of milk of lime and active carbon, likewise in installation in Kraków [10, 11].

4. Scrubbers

Scrubbers are devices, that can remove gaseous and/or particle pollutants from exhaust gases from industrial processes. Absorption is a process, in which particles in are diffusively transported from the cleaned gas (absorbate) to the liquid, called the absorbent. In devices called absorbers this process occurs continuously, and it's often accompanied by chemical processes. The increase of the interfacial surface and diffusion speed can speed up the absorption process [12]. We can distinguish physical absorption or physical absorption with chemical reaction, that is chemisorption. Physical absorption is a reversible process. The reversible process is called desorption, and the absorbed component is removed from the liquid. For balance of the process following parameters have influence: temperature, pressure and concentration. High pressure, high concentration of component in gaseous phase and low temperature favor the process [4].

The surface scrubbers are used in processes that involve easily soluble gases. There are three main types of scrubbers:

4.1. Packed tower scrubbers

Packed tower scrubbers are the most commonly used scrubbers. They are filled with either fixed or fluidized bed. They are characterized by low gas pressure drop and the fact, that the bed is not poured with the absorbent. The retention is low in this kind of scrubbers, the liquid is poorly distributed and the bed surface is used only in a small extent. In fluidized bed scrubbers, the bed usually consists of hollow spheres made of synthetic material, resistant to the processes occurring inside the scrubber. Raschig's, Lessig's, Pall or Białecki's rings can be also used, as well as Berl saddles and other types of fillings. The density of such packing should be lower than the density of the liquid. The bed is fluidized by the cleaned gas from flowing upstream, and it's moistened by the liquid that flows concurrently to the gas. Three-phase fluidization increases the contact area, and as a result the efficiency of the whole process is increased. Liquids, that are contaminated with solid particles, can be used in fluidized bed scrubbers. Such processed are characterized by low pressure drop, lower than 2 kPa [4].

4.2. Spray nozzle scrubbers

Spray nozzle scrubbers are a type of scrubbers without any packing. The absorbent is sprayed by spray nozzles and while flowing down it contacts with cleaned gas. There are three main types of spray nozzle scrubbers: countercurrent, concurrent and crosscurrent. They differ by the direction of the liquid and gas flows: in countercurrent absorbers, the sprayed liquid flows in the direction that is opposite to the flowing gas. In concurrent scrubbers, the liquid flows in the same direction as the gas, and in crosscurrent scrubbers the sprayed liquid is directed perpendicularly to the gas. Sometimes also the reverse flow can be used- in such case, which is a combination of concurrent and countercurrent flows, the flowing liquid is reversed inside the device [4]. Spray nozzle scrubbers have a simple structure, and therefore are resistant to clogging by the dusty gases. Some problems may occur during the liquid recirculation because of possibility of blocking of spray nozzles, and it can lead to the premature wear. The efficiency of processes occurring in spray nozzle scrubbers is low, however they are frequently used because of their simple design, high reliability, relatively low exploitation costs and low hydraulic resistance [3].

4.2.1. Venturi scrubbers

In Venturi scrubbers, the absorption process takes place mainly in the throat. The length of the throat depends on the process. Such scrubber consists of three main sections: converging section, in which the gas and liquid are concurrently introduced, then directed to the throat, in which the velocity of the gas dramatically increases. This high velocity of the cleaned gas causes the formation of small liquid droplets- the contact area between absorbent and absorbate increases. In the diverging section the velocity decreases. This kind of scrubbers can be used to remove gaseous and particulate pollutants, however the particle removal efficiency is higher than the efficiency of gaseous pollutants removal.

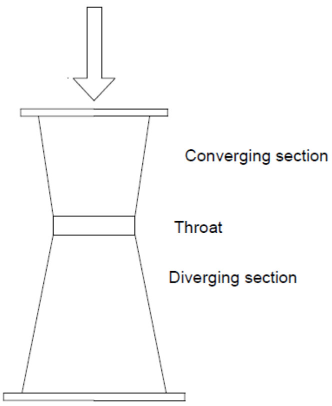

Fig. 3.2. Venturi scrubber [13].

4.3 Plate towers

Plate towers are column scrubbers, in which many plates (or trays) are placed horizontally. The principle of this process is based on the gas bubbles flow through the gaps in the plates, which are covered in absorbent liquid [14]. The liquid can be directed concurrently, concurrently or cross currently to the gas, and each tray is flooded.

Before entering the scrubber, the gas is cooled and moistened. This kind removes gaseous pollutants very effectively, and can be also used to remove particles, however, it is not recommended to use it only for particle removal. Many types of plates can be used in plate towers. The most commonly used types are sieve plates with round gaps, impingement plates, in which the gaps are similar to sieve plates with the impaction target is added above every gap, and bubble-cap plates, which forces the gas to form bubbles for any liquid to gas ratio [13].

5. Selection of absorber

Selection of absorber must be based on knowledge about absorber's principle of work, their ability of effective gas cleaning and costs of the cleaning. Output quantities of design are usually: gas stream, gas composition and temperature and demanded cleaning efficiency. Optimal design should provide, with minimal cleaning cost, demanded cleaning grade in exploitation period. Following steps take part in designing process:
1) selection of dissolvent – absorbent,

2) definition of balance data,

3) definition of values and parameters of the process (material and energy balance),

4) selection of absorber's construction,

5) definition of column's diameter or other characteristic dimension,

6) definition of height, contact space or amount of plates,

7) calculation pressure decrease [4].

Moreover one has to select essential and adequate interior equipment for absorber and auxiliary devices, such as: sprinkling nozzles, their amount and way of arrangement, kind of filling and way of its sprinkling, kind of plate, stream of liquid and gas inside and many other details. Besides there in the installation there are auxiliary devices e.g. ducts and pipelines, fans and pumps, valves, dosage systems, control-measuring systems.

Selection of appropriate construction material has deciding meaning for absorber's efficient exploitation with not very high costs. Material is selected depending on kind of pollution, used liquid, temperature and forming cleaning products [4].

Most typical pollutions removed by absorption method are highly corrosive. Hence, the absorbers are made from acid resistant steel, constructional steel with equivalent lining, special alloy steel, ceramic materials, plastics strengthened with glass fibre [4].

6. Conclusions

In the article there are presented methods of desulfurization of flue gases from waste incineration processes. The methods are based on absorption processes. Desulfurization process take place in scrubber, which is often placed after a deduster. In wet lime method there is produced gypsum, that can be used in building industry. Advantages of this method are: high efficiency, cheap sorbent, low exploitation costs and useful product. Disadvantages of this method are: high investment costs, wet product, corrosion and erosion of the installation [3]. Such method is used in incineration plant in Dąbrowa Górnicza and Jedlicze [7, 8]. In the semi-dry method the efficiency is lower than in the previous one, however there is lack of sewers and the product is dry, which is better from the waste management point of view, the construction is simple and there is lower energy consumption [6]. This method will be applied in newly formed incineration plants in Kraków, Ruda Śląska and Łódź [9, 10, 11]. Reactions in dry methods are proceeded less efficient than in the previous methods, however the installation is simple and we obtain dry product [6].

The devices used in flue gases desulfurization are absorbers. The most often used are packed tower scrubbers, filled with either fixed of fluidized bed. The bed is fluidized by the cleaned gas flowing upstream, and it's moistened by the liquid that flow concurrently to the gas [4]. Other kind of scrubbers are spray nozzle scrubbers, without any packing. The absorbent is sprayed by spray nozzles and while flowing down it contacts with cleaned gas [4]. There are also plate towers, which are column scrubbers, in which many plates are placed horizontally. The gas bubbles flow though the gaps in plates, which are covered in absorbent liquid [14].
The selection of absorber is based on the knowledge about absorber's principle of work, ability of effective gas cleaning and costs of the cleaning. The optimal design should guarantee demanded efficiency with minimal costs

[4].

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