STUDIU PRIVIND STADIUL ACTUAL ȘI TENDINȚELE VIITOARE ALE TEHNOLOGIILOR DE DESULFURARE A GAZELOR DE ARDERE: REVIEW

STUDY ON CURRENT STATE AND FUTURE TRENDS OF FLUE GAS DESULPHURIZATION TEHNOLOGIES: A REVIEW

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Fossil fuels used in thermal power plants contain significant amounts of sulfur. At burning, about 95% of the sulfur is converted to sulfur dioxide (SO_2), which reacts with the particles of water in the atmosphere, forming acid rain under normal conditions of temperature and pressure. Sulfur dioxide, through its annual emissions, is the main gas pollutant, which is why over the last 80 years has been a concern for the development and streamlining of desulphurization processes. The flue gas desulphurization can be done both by wet or dry process. The most widespread process is wet desulphurization of limestone or lime, accounting for about 85% of all desulphurization processes. The paper presents the current state of the desulphurization technologies in the world, their advantages and disadvantages, as well as the future trends in this field.

Combustibilii fosili utilizaţi în termocentrale, conţin cantităţi semnificative de sulf. La ardere, aproximativ 95% din cantitatea de sulf se transformă în dioxid de sulf (SO_2) care, reacţionează cu particulele de apă din atmosferă, formând ploi acide în condiţii normale de temperatură şi presiune. Dioxidul de sulf, prin cantităţile anuale emise în atmosferă, este principalul poluant gazos, motiv pentru care există de peste 80 de ani o preocupare pentru elaborarea și eficientizarea proceselor de desulfurare. Procesul de desulfurare a gazelor de ardere se poate realiza atât pe cale umedă, cât și uscată. Cel mai răspândit procedeu este desulfurarea umedă a calcarului sau varului, reprezentând circa 85% din totalitatea procedeelor de desulfurare. Lucrarea prezintă situația curentă a tehnologiilor de desulfurare din lume, avantajele și dezavantajele acestora, cât și tendințele viitoare din acest domeniu.

Keywords: *limestone, flue gas desulphurization, sulphur dioxide, FGD-gypsum, fly ash.*

1. Introduction

Combustion of fossil fuels leads to discharging into the atmosphere significant volumes [1, 2] of gaseous sulphur oxides. Sulphur dioxide is a major pollutant and have a significant impact on human health. High concentrations of sulphur dioxide in atmosphere can influence the flora and fauna. Moreover, SO_2 emissions represent a precursor for acid rain and atmospheric particles [3, 4]. Particulate matter is made of very small solid particles and very small liquid drops that give to the flue gases their smoky appearance [5].

As the flue gas desulphurization (FGD) technology advanced in time, some processes were removed from the market because of economic and technical reasons, while some others developed, becoming more mature, fact proven through: a higher efficiency rate of desulphurization, the use on a large scale and a simplified technological process [6].

If the beginnings of desulphurization found in the first development line countries like USA, UK, Germany, Japan, after the 90's a lot of developing countries (especially Asian ones) started research and application on desulphurization processes [7].

2. Flue gas desulphurization processes - FGD

Desulphurization process removes sulphur or sulphur based components from solids, liquids and gases. Most of all, desulphurization refers to removing sulphur oxides from flue gas. Desulphurization is necessary because of environmental regulations regarding SO_2 emissions [8]. Depending on the final co-product, FGD processes are divided into those whose co-product is disposed on landfill, and those with a commercially useful co-product. Environmental requirements imposed by the current legislation led to research regarding valorisation of waste from thermal power plants (synthetic gypsum and ash). A field with large valorisation possibilities of these waste is represented by the construction materials [9-17].

In almost all FGD systems, SO_2 is extracted from flue gas through a reaction with an alkaline substance to produce sulphite or sulphate.

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FGD process is based on the contact of the flue gas with an absorbing substance (absorbent/reactive) that reacts and/or absorbs SO_2 and other acid gases (SO_3, HCl, HF). Based on the scientific literature [18], FGD technologies can be classified in regenerative and non-regenerative (one pass).

Regenerative processes – the used absorbent is recycled after thermal or chemical treatment generating concentrated SO_2, that is further transformed, usually, in elementary sulphur. These complex processes need high investment costs and a higher energy consumption during exploitation. These processes are not used on a large scale for FGD mainly because of the costs and very low commercial value of sulphur.

Non-regenerative processes *(one pass)* – the absorbent is not recycled. During time these were and are the most used FGD technologies at industrial scale.

Depending on the aggregation state of the used absorbent, FGD technologies can be classified as:

-wet processes (suspension or solution; the discharged gases are water saturated);

-semi-dry processes (controlled humidification, the wet absorbent becomes solid in SO_2 absorption process);

-dry processes (water is not used at all, zero humidification).

A classification of desulphurization processes can be seen in Figure 1, being based on the most common processes used on industrial scale.

2.1. Dry process

Sorbent Injection (SI). In the case of dry systems (Fig. 2) with alkaline absorbent compounds, these are either injected in the gas flow, or the gas flow is passed through an absorbent layer. Typical sorbents include sprayed calcium carbonate ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$). In the burning point, heat addition determines the generation reactive particles of CaO through sorbent calcination. The surface of these particles [19] reacts with SO_2 in the gas flow to form calcium sulphite ($CaSO_3$) and calcium sulphate ($CaSO_4$). Reaction products are further retained together with the flying ash by the control device of micro particles, usually an an electrostatic precipitator (ESP) or a fabric filter (FF). The dry system [20] depends mostly on the adsorbent that can be very fine or very porous. The reactions of SO_2 removal through sorbent injection in the burning point are as follows:

$$CaCO_3 + heat \rightarrow CaO + CO_2 \text{ or } Ca(OH)_2 + heat \rightarrow \rightarrow CaO + H_2O \quad (R1)$$

$$CaO + SO_2 + ½\, O_2 \rightarrow CaSO_3 + heat \quad (R2)$$

Taking into consideration the characteristics of this process, industrial use of dry technology is not very widespread and its applications are limited. Depending on the supply point of alkaline substance, different types of reagents can be used (limestone, lime or hydrated lime). As it was shown in [21], lime/gypsum (L/G) molar ratios are higher, fact that leads to a low

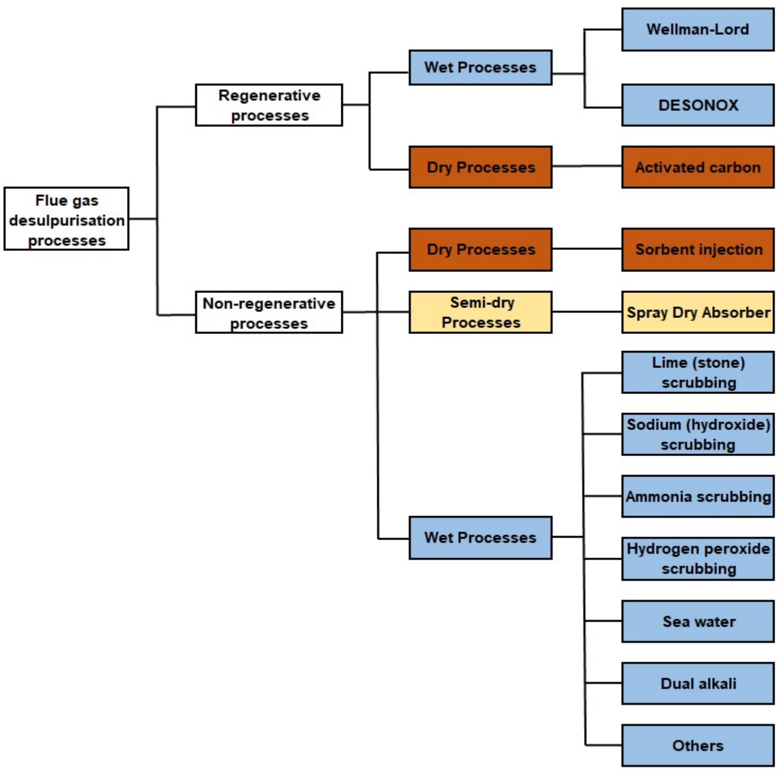

Fig. 1 - FGD process classification / *Clasificarea proceselor de desulfurare a gazelor de ardere.*

desulphurization efficiency. That is why desulphurization installations through dry process are decreasing, especially because of worldwide stricter environmental legislation.

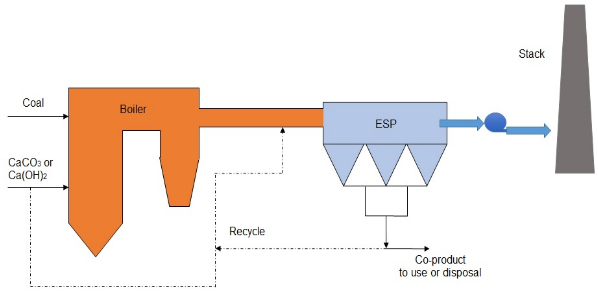

Fig. 2 - Typical dry FGD process / *Schema tipică a procedeului uscat.*

However, lately dry process developed as reduction process [22] for multiple pollutants (SO_3, HCl, HF and Hg), thus becoming an alternative to the wet process for thermal power plants and other steel and iron manufacturing plants.

2.2. Semi-dry process

Semi-dry processes are similar to the dry ones [23], except that water is added to create a thin liquid layer on the adsorbent particles, in which SO_2 is dissolved, thus enhancing the reaction with the solid. Solid product is collected in dust collection equipment in order to be sold or stored. The most known semi-dry processes are CDS (Circulating Dry Scrubber, also known as CFB - Circulating Fluidized Bed) and SDA (Spray Dry Absobtion).

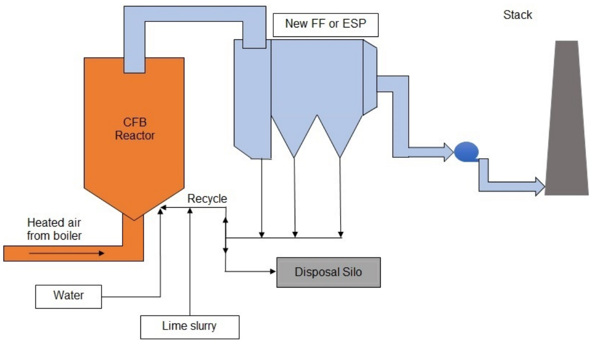

Fig. 3 - Typical CDS-CFB process / *Schema tipică a procedeului CDS-CFB.*

CDS Process (Circulating Dry Scrubber) – CFB (Circulating Fluidized Bed). CDS is a semi-dry FGD process in which flue gas is passed through a mixture of lime(stone), products of reaction and fly ash (depending on the location of the filling) on a CFB (Fig. 3). SO_2 is extracted in a proportion of up to 99%, all SO_3 and HCl being also extracted. CFB semi-dry process is a relatively simple technology, limestone or hydrated lime being usually used as adsorbent in CFB process and injected at the reactor base. Water is also added to moist the flue gas, thus improving SO_2 and macro particles extraction. The reactions that take place in the CFB process when limestone is used are presented as follows.

$$CaCO_3 \rightarrow CaO + CO_2 \quad (R3)$$

$$CaO + \frac{1}{2}O_2 + SO_2 \rightarrow CaSO_4 \quad (R4)$$

CFB semi-dry process has almost unlimited turndown capability and is flexible regarding rapid changes in inlet SO_2 concentrations. Operational costs of CFB process are relatively high [24]. Compared with wet LSFO (forced oxidation of limestone) process, CFB process has lower investment costs, and compared with semi-dry SDA process, investment costs are approximately at the same level.

The flue gas enters through the bottom of the venturi shaped absorber and the acid gases such as SO_3, SO_2, HCl, HF and partially CO_2 are removed by hydrated lime. The optimal reaction temperature, which is 20 to 30 °C above the wet bulb temperature, is achieved by water injection directly into the bottom of the fluidized bed. The reaction products are entrained to the top of the absorber and collected in the downstream precipitator, which may be a fabric filter (FF) or an electrostatic precipitator (ESP) without any difference in desulphurization efficiency. The characteristic of this process is represented by the venturi section, where the flue gas acceleration takes place. In the last years design changes have been successfully implemented for the venturi section and water injection system [25-29], for significantly decreasing consumption of lime suspension.

SDA process - Spray dry absorption.

Concentrated lime paste is injected in flue gases in order to extract SO_2, SO_3 and HCl. The chemical reactions that take place in the semi-drying process with spraying are similar with the ones from the CFB process and the final product is a dry dusty mixture of calcium components that needs storage (Fig. 4).

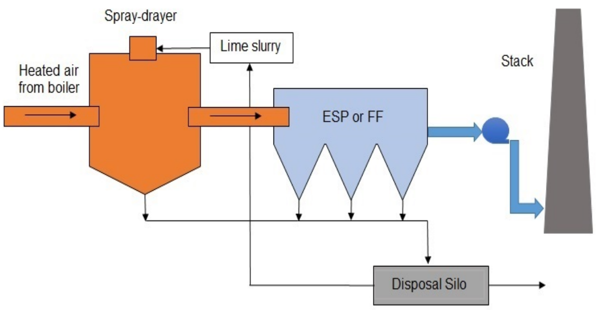

Fig. 4 - Typical SDA process / *Schema tipică a procedeului SDA.*

Low use of SDA process, compared with CFB process, is due to higher operational costs because of higher use of adsorbent and of product storage costs.

Although semi-dry processes are less

used compared to the wet ones, SDA and CDS processes present many advantages than LSFO wet process: consumption with approximately 60% less water, lower space for installation, lower auxiliary energy consumption, lower investment costs, higher efficiency of SO_3, HCl, Hg and other acid gases removal. Regarding the disadvantages of semi-dry processes, we observe: lower efficiency of removal SO_2 emissions, although modern CDS systems can reach a 98% efficiency [30]; lack of a selling co-product; higher operation costs because of reagents used and maintenance costs for dust removal equipment.

2.3. Wet process

General technologies of FGD using wet processes need an alkaline reaction agent (limestone, lime, caustic soda, ammonia, sea water) [31]. The most known wet desulphurization processes are: forced oxidation of limestone - LSFO (L/G), (W-L), (MEL) process, seawater FGD [32] and ammonia process.

Limestone forced oxidation (LSFO or L/G – Limestone/gypsum process). Even from the ’80s, LSFO is the top technology in flue gas desulphurization through wet process [33], as well as in general. In LSFO process (Fig. 5), known as L/G process (limestone/gypsum), flue gases pass through a heat exchanger and enter in FGD scrubber where SO_2 is removed through direct contact with a dense aqueous limestone suspension, in which limestone must contain more than 95% $CaCO_3$. In the absorption installation fresh limestone suspension is continuously introduced. Moreover, at this process all HCl that exists in flue gas [34] is extracted. Clean gas leaves the absorbent layer through moist eliminator and then is discharged through the stack. For a higher efficiency of mist removal, good washing techniques are needed and a lower flue gas speed than their critical speed. The reaction products are extracted from the absorption installation and transferred for dehydration and further processing. Residence time of limestone solution in the scrubber tower is generally 3-5 min.

A basic process and possible alternative in selecting the technological process is the oxidation of calcium sulphite or bisulphite (generated in SO_2 reaction with limestone/limestone). This can be produced through forced oxidation or through natural oxidation. Oxidation conditions have an important influence on the quality of resulted co-product.

The most used absorbent is limestone because of its wide availability and low price. Limestone properties have an important influence on the efficiency of FGD system in general and on the scrubber performance in particular: high content of calcium carbonate; low content of Al, F and Cl; reactivity (dolomite fraction); size distribution. Lime can also be used (MEL process), but it presents the risk of carbonation. Adsorption yield of SO_2 is the same. From the wet technology, gypsum sludge or calcium sulphate /sulphite mixture and flying ash (from thermal power plant) results.

The quality of co-product depends on the type of oxidation. Wet scrubber technology with lime/limestone needs big land surfaces for disposal of sludge. If the quality of the gypsum is good, then the co-product is marketable. If the gypsum contains big quantities of fly ash or sulphite, it cannot be used and it must be disposed at an appropriate (non-hazardous waste) landfill.

Calcium sulphite is oxidized by the air injected in the scrubber, dehydration is easy because the gypsum crystals are relatively big. Primary dehydration is done usually in hydro cyclones being followed by a secondary dehydration in filters or centrifuge. The final product, that contains approximately 90% solids, is easy to handle and easy to sell especially like gypsum for plaster, cement, gypsum-board manufacturing, replacing natural gypsum. Basic chemical reactions in case of this process are presented below.

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \quad (R5)$$
$$CaSO_3 + O_2 + 2H_2O \rightarrow CaSO_4{*}2H_2O \quad (R6)$$

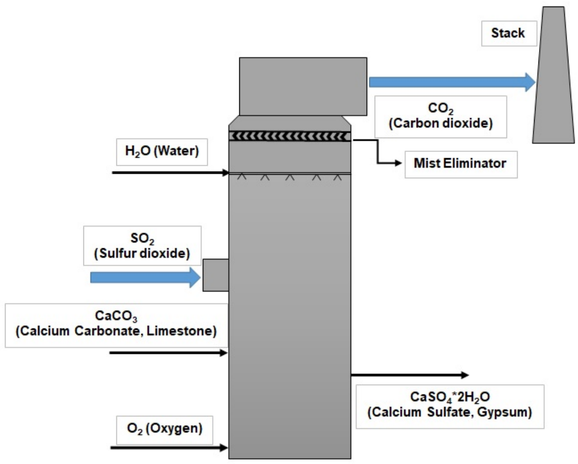

Fig 5 - LSFO typical process / *Procedeul tipic de oxidare forțată a calcarului.*

FGD wet process has an optimal operation at a *p*H ranging between 5 and 6. At *p*H < 4, SO_2 balance pressure increases, and the absorption rate of gases decreases slowly towards 0. Where *p*H values are > 6.3, we meet cases where the scrubber has been affected by $CaSO_3$ precipitation. When *p*H is below 6.3, $CaSO_3$ dissolution is possible [35]. During the process, impurities might collect in the generated sludge. Impurities concentration of the adsorbent material might increase as a result of its recycling in the process. To reduce this inconvenient a water treatment system of the adsorbent material is used.

LSFO process needs high investment costs (but not as high as the wet process based on ammonia or the Wellman-Lord process). Although LSFO process is similar [36] to wet desulphurization process with lime (MEL), the operation costs are lower because limestone is cheaper than lime.

In thermal power plants from Germany and Holland tests have been performed that indicated that at least 40% of the water used at desulphurization can be recovered [37], transforming those thermal power plants from water consumers into producers. Quality of recovered water is high, it can be used not only for demineralization in industry but also for public use.

Wet technology has the following advantages: very high desulphurization efficiencies, low operation costs of the installation, limestone is a cheap raw material from which synthetic gypsum can result. On the other hand, as disadvantages we can mention: high investment costs, high water consumption, covers wide areas and, maybe the most important because of process chemistry, low efficiency for metals Hg, and acid gases like SO_3 and HF removal.

Ammonia FGD. Desulphurization process based on ammonia [38-40] is similar with LSFO process. General reactions of this process are as follows.

$SO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_3$ (R7)
$(NH_4)2SO_3 + ½O_2 \rightarrow (NH_4)_2SO_4$ (R8)

Wet technology with ammonia can be attractive from economical point of view compared with LSFO. The benefits of this technology are the following: marketable co-product, lower investment and operation costs. Moreover, the wet process based on ammonia does not produce additional CO_2 emissions.

Seawater Process (SWFGD). This process dates from the beginning of '70s when research conducted by Berkley [41] demonstrated the feasibility of using seawater in desulphurization process. Because of obvious reasons, this type of installation can be used only on coastal areas. Seawater usually has a *p*H of 7.6-8.4, thus allowing neutralization of flue gases that come with acidic *p*H. Flue gases come in contact with seawater in the absorption area and before discharging them at the stack they pass through a mist eliminator (Fig.6) [42].

In wet flue gases desulphurization systems conditions for very aggressive corrosion are usually met. These are characterized by chemical hazards, by very high temperatures and erosion. Thermal power plants with FGD systems will need to improve their processes for maximizing the efficiency [43] of SO_2 reduction either through

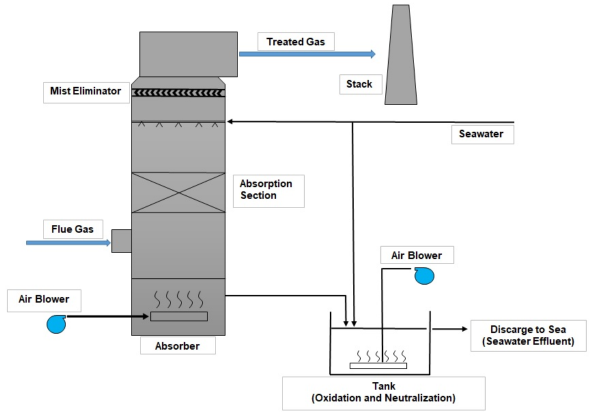

Fig. 6 - Typical seawater FGD process / *Desulfurarea cu apă de mare.*

adding secondary absorbents either through modernizing existing absorbents.

3. Efficiency and co-products

Efficiency of SO_2 removal in a FGD installation can be characterized through "desulphurization rate" (or "desulphurization efficiency") that means ratio between sulphur amount that is no longer generated (as SO_2) into the atmosphere by a combustion installation in a certain period of time and the sulphur amount contained in the solid fuel introduced in the combustion installation and that is used in the installation in the same period of time. When choosing a desulphurization technology, it is necessary to take into consideration technical (desulphurization efficiency and reliability), economical (investment costs and operational costs) and commercial (reliable supplier, proven technology and warranty from supplier) aspects [44].

During time, wet technology showed the most significant efficiencies regarding SO_2 removal from flue gas. In the last years, differences between processes regarding efficiency were decreased. Thus, efficiencies of up to 97% for dry process [45], 95-98% for CDS(CFB) process [46] and 90-95% for SDA process [47] were reported. Approximately 80-85% of the worldwide FGD installations, are using LSFO wet process, and its efficiency might reach after the most recent data +99% [48-53].

An efficiency example can be given using data from Ploscaru *et al.* [54]. All four energetic blocks from below belongs to Rovinari power plant from Romania and have the same capacity (878 MWt) [55]. As shown in Table 1 below, energetic block 3 and 6 have a wet FGD system, while energetic block 4 and 5 have no FGD system.

As we can see from the monthly averages, SO_2 removal efficiency of blocks 3 and 6 in 2012 was around 95% using a wet FGD system (LSFO).

Table 1

SO_2 emissions from block 3, 4, 5, 6 at Rovinari power plant / *Emisii de SO_2 la blocurile energetice 3, 4, 5, 6 la termocentrala Rovinari*

Month	Energetic block 4	Energetic block 5	Energetic block 3	Energetic block 6
	SO_2 emissions, mg/Nm^3			
January	4580.1	4595.9	244.6	163.1
February	4918.9	5454.2	247.9	309.3
March	4743.8	5730.9	195.5	280.6
April	4130.3	N/A	228.6	258.0
May	4480.6	5063.4	229.9	256.4
June	4976.9	5134.4	226.4	271.1
July	4951.9	5169.3	254.3	258.2
August	N/A	4794.6	277.5	275.9
September	N/A	6569.2	281.3	312.7
October	N/A	6042.3	268.4	323.6
November	N/A	6028.0	264.2	321.0
December	N/A	5774.8	284.0	429.0
Monthly average	**4683.2**	**5487.0**	**250.2**	**288.2**

Table 2

FGD Classification and co-products based on process / *Clasificarea si co-produsele desulfurarii functie de procesul utilizat.*

	Dry	Semi-Dry	Wet
Characteristics	Dry powder-Reactor-Dry powder	Slurry or solution-Reactor-Dry powder	Slurry or solution-Reactor-Slurry or solution
Main reactor	Dry Injector	Semi Dry Reactor	Wet Scrubber
Application	Small / Medium scale		Large scale
Agents	Mg, Ca, Na compounds		Ca, Mg, Na compounds
Coal % Sulfur preference	<3%		>3%
Removal efficiency	up to 95%	up to 98%	up to 99%
Water usage	Minimum	Medium	High
Waste water treatment	unnecessary		necessary
Byproduct	Calcium sulfite and sulfate		Gypsum, Ammonium Sulfate, Sodium Bisulfite
Operation cost	High	Medium	Low

Desulphurization installations with seawater have the same efficiency as LSFO [56]. Also on wet process we encounter efficiencies of 95-98% at ammonia process [57] and Wellman-Lord process [58, 59].

The quality of FGD co-products (Table 2) is heavily correlated with coal quality and with desulphurization techniques used. The co-products from dry or semi-dry desulphurization process are in majority of cases dry, meaning easier to handle and store compared to the ones that are generated by the wet process. Most often we can encounter these co-products in construction materials manufacturing, mine applications, highway building or agriculture [60-63].

An advantage of wet process LSFO is that it has as co-product synthetic gypsum [64], sellable material that has the same properties as natural gypsum and that has its place on the market of construction materials replacing successfully natural gypsum. One of the benefits associated to use of synthetic gypsum in cement industry is that dependency of natural raw material will decrease [65]. Thus, synthetic gypsum can replace successfully natural gypsum in the most common use of it [66]. Synthetic gypsum obtained after flue gas desulphurization from thermal plants [67-74] is used as additive at Portland cement manufacturing, construction materials industry, agriculture and others.

4. Conclusions and FGD future trends

Data from the literature shows that the wet FGD process of limestone / lime is the most widely spread process due to high desulphurization performance and low operating costs. At the same time, the efficiency of wet installations is higher than dry process.

The trend with regard to wet FGD process is to improve existing installations with a 90% desulphurization rate up to 99.9%. Energy producers will have to modify their existing installations either by adding secondary absorbers or by introducing modern nozzles, and those without FGD systems will need to consider installing systems that can achieve a desulphurization efficiency of over 99%. Another aspect on what developers focuses on FGD technology is to reduce the need for water for the wet process. Reducing the need for water is an acute problem especially in areas affected by drought.

Increasing demand for electricity and dependence on fossil fuels will focus in the future on technologies to reduce emissions of many pollutants. The global market for FGD systems and services has seen significant growth in recent years, and this growth will continue in the years to come.

The legal constraints on the environment, the increase in SO_2 concentration in the atmosphere and the increasing number of coal-fired thermal power plants will be the key factors influencing the global FGD market. Currently, the developers of FGD technologies focus their attention on the resulting co-products, seeking their recovery and reuse.

Regarding future trends in LSFO wet process who is the most widespread, it is upgrading and optimizing the process, and designing smaller installations to lower investment costs. FGD installations of the future will have to meet the following criteria:

- low water consumption;
- high efficiency removal of SO_2 and SO_3;
- heavy metals removal;
- low investment, operating and maintenance costs;
- high reliability;
- co-products which can be sold or can be used.

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