

SEAWATER AS A REAGENT IN THE FLUE GAS DESULPHURISATION PROCESS

MORSKA VODA KOT REAGENT V PROCESU REAŽVEPLJEVANJA DIMNIH PLINOV

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Keywords: Sea Water, Flue Gas Desulphurisation, Cleaning of Flue Gases, Sulphur Dioxide, Industrial Coastal Areas, Emissions

Abstract

Sulphur dioxide is a poisonous substance that is vastly formed in the process of fossil fuel burning inside the steam boiler of a thermal power plant, or any other industrial plant that uses fossil fuels as a prime source of energy. The technology involved in cleaning the sulphurous component from the raw, uncleaned flue gas flow in fossil fuel-based power and industrial plants is a form of technology that has been present for the last three decades and is constantly evolving in its characteristics and performance to deliver the highly-efficient flue gas cleaning procedure. The standard and technological mature technical solutions for flue gas desulphurisation of untreated flue gases are comprised of dry, semi-dry, and wet flue gas desulphurisation processes. The most frequently used solution, as well as that most applicable to most existing and new fossil fuel-based thermal power plants, is the wet flue gas desulphurisation process. The aforementioned wet cleaning process may be limestone-based (LFOS – Limestone Forced Oxidation System) or magnesium-based (MEL – Magnesium Enhanced Limestone). The paper focuses on the remaining wet flue gas desulphurisation procedure, one which is neither widely-present nor known within the industry – the SWFGD (Seawater Flue Gas Desulphurisation) process. This process has numerous advantages, including the presence of a costless reagent in vast amounts (seawater), the optimisation of the plant's design, and those linked to operational costs.

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We will present the flue gas cleaning process and its chemical aspects through a description of the process. We will then explore the main advantages and disadvantages of the corresponding process, as well as undertaking and presenting a comparative analysis between the main three wet flue gas desulphurisation processes (LFOS, MEL & SWFGD), taking into consideration all crucial points of each aforementioned wet flue gas cleaning process. As stated before, the main intention of wet desulphurisation processes is to remove the acid components from the untreated flue gas flow. In the process of doing this, the formation of by-products and effluent occurs, both of which have different impacts on the environment. Within the scope of this article, we will evaluate the environmental impact of the resulting by-products of each of the corresponding wet flue gas desulphurisation processes.

Povzetek

Žveplov dioksid je toksična snov, ki večinoma nastane pri izgorevanju fosilnih goriv v parnem kotlu termoelektrarne ali katerega koli drugega industrijskega obrata, ki uporablja fosilna goriva kot glavni vir energije. Tehnologija za čiščenje žveplove komponente iz neočiščenega toka dimnih plinov v termoelektrarnah in industrijskih obratih, ki delujejo na fosilna goriva, je prisotna že tri desetletja in se nenehno razvija v svojih lastnostih in zmogljivosti, da zagotovi učinkovit postopek čiščenja dimnih plinov. Standardne in tehnološko zrele tehnične rešitve za razžveplanje dimnih plinov so sestavljene iz suhih, polsuhih in mokrih postopkov razžveplanja dimnih plinov. Najpogostejši in najuporabnejši za večino obstoječih in novih termoelektrarn na fosilna goriva je postopek mokrega razžveplanja dimnih plinov. Zgoraj omenjeni postopek mokrega čiščenja je lahko na osnovi apnenca (LFOS – Limestone Forced Oxidation System) ali na osnovi magnezija (MEL – Magnesium Enhanced Limestone). V prispevku se bomo osredotočili na preostali postopek mokrega razžveplanja dimnih plinov, ki je v industriji premalo prisoten in poznan – postopek SWFGD (Sea Water Flue Gas Desulfurization). Ta postopek ima številne prednosti, kot so poceni reagent v velikih količinah (morska voda), optimizacija zasnove naprave in operativni stroški. Preko opisa postopka bomo predstavili potek čiščenja dimnih plinov in njegove kemijske vidike. Izpostavili bomo glavne prednosti in slabosti tega postopka ter izpeljali primerjalno analizo med glavnimi tremi postopki mokrega razžveplanja dimnih plinov (LFOS, MEL & SWFGD), ob upoštevanju vseh ključnih točk vsakega omenjenega mokrega postopka. Glavni namen razžveplanja dimnih plinov je odstraniti kislinske komponente iz neočiščenega toka dimnih plinov. Pri tem je prisotno nastajanje stranskih produktov in odpadka, ki imajo različen vpliv na okolje, zato bomo v okviru prispevka tudi ovrednotili okoliške vplive nastalih stranskih produktov posameznega postopka mokrega razžveplanja dimnih plinov.

1 INTRODUCTION

Due to the constant growth of the world's population and, consequently, the growing demand for electricity, more and more energy plants are being built for the purpose of producing electricity. Despite the awareness that the combustion of fossil fuels releases greenhouse gases into our atmosphere, ultimately leading to the phenomenon known as the greenhouse effect, fossil fuel thermal power plants remain one of the key pillars of electricity production in the electricity supply sector. In addition to greenhouse gases, thermal power plants also emit other forms of emissions into our atmosphere, including sulphur dioxide (SO₂). In high concentrations, sulphur dioxide emissions can be harmful to human health, affecting our living environment and plants, as well as other specimens within the environment itself. Over the last 30 years, the technology

involved in cleaning and removing acidic components from flue gases has advanced to a point where it can offer industrial and energy plants three ways to clean flue gases, namely through dry, semi-dry and wet flue gas cleaning processes. Each of these processes has its advantages and disadvantages, and the key to choosing the right flue gas cleaning technology is to carefully consider all factors that affect the technical, economic, and environmental parameters of the operation of the flue gas desulphurisation plant. This article covers and presents a basic record of wet flue gas cleaning technology using seawater as a reagent. [1] Such flue-gas desulphurisation plants are particularly suitable for locations where industrial or thermal power plants have access to large quantities of seawater. [2]

2 KEY MARKETS OVERVIEW

Flue gas cleaning technology was introduced to the market in as early as 1970. The SWFGD process was first handed over to a Japanese client for commercial use in 1978 at an industrial plant for the production of chemicals. This was followed by a second SWFGD plant in 1988 at an oil refinery in Norway. [3] Despite good flue gas cleaning results and highly competitive investment and operating costs compared to other processes, this branch of flue gas cleaning technology has not gained a strong foothold in the market. [4] In 2000, the U.S. Environmental Protection Agency published an analysis of the use of FGD technologies.

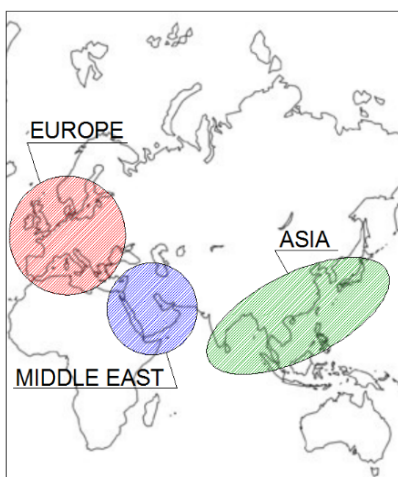


Figure 1: Areas where FGD technology is still in demand due to retrofit or green-field projects

The results of the analysis showed that the share of SWFGDs represented only 0.6% of all desulphurisation systems in industrial and thermal power plants. Recently, we have seen an increase in demand and the installation of new SWFGD plants, mainly in coastal areas of Europe, Asia, and the Middle East (Turkey, Saudi Arabia, Iran, Iraq, Kuwait...). [5] Emphasis in the development of flue gas cleaning technology with the use of seawater mainly centres on reducing the space required for the installation of the plant, extending the life of the plant, and improving its design and operation to achieve better efficiency and reduce investment and operating costs. [6]

3 PROCESS DESCRIPTION

The SWFGD plant consists of two main components. The first part is the system for the absorption of sulphur dioxide (SO_2) and is intended to reduce the emissions of sulphur dioxide in the exhaust flue gases from the industrial or thermal power plant in question. The second part of the system is the process for the handling and treatment of used seawater before its discharge back into the sea. The principle of operation of SWFGD within a thermal power plant is schematically presented in Figure 2. Flue gases are channelled from the exit of the steam boiler to the electrostatic filter, the latter of which has the task of removing solid dust particles from the flue gases. Once the flue gases have passed through the electrostatic precipitator, they are further routed to the heat exchanger before entering the absorption vessel. In the heat exchanger, heat is transferred from hot, uncleaned, incoming flue gases to cold, cleaned outgoing flue gases from the absorption vessel. The cooled, uncleaned flue gases from the heat exchanger pass through into the absorption vessel. Here, the actual flue gas cleaning process also takes place.

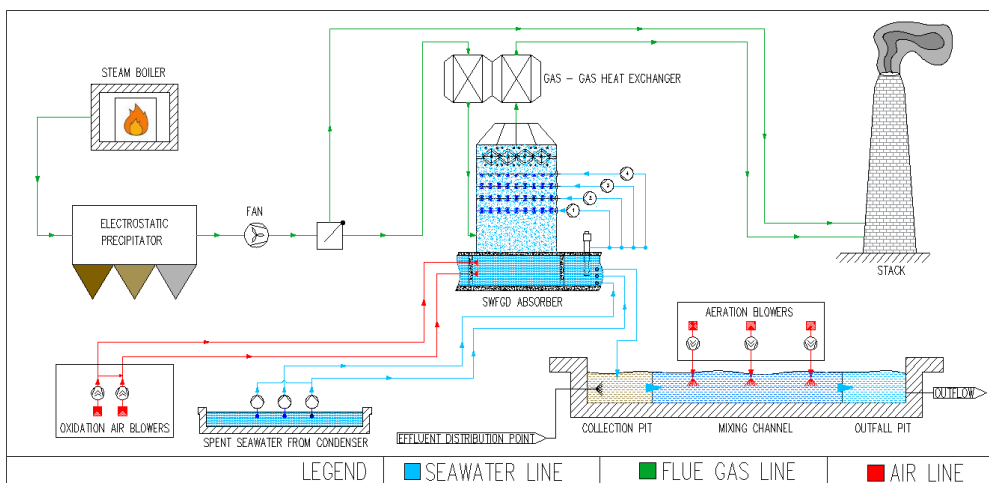


Figure 2: Principle of operation of the SWFGD within the thermal power plant

In the absorption vessel, the flue gases from the steam boiler and the reagent - seawater - come into contact. Most often, seawater is sprayed counter-currently through the flue gases. This allows optimal contact between the acidic components in the flue gases and the basic components in the seawater. The absorption zone in the absorption vessel consists of perforated steel plates that forcibly conduct flue gases so that contact between the aqueous and gaseous medium is maintained for as long as possible, consequently rendering the process more efficient. Cleaned flue gases are also conducted through a droplet separator that dries the flue gases. From the absorption vessel, the cleaned flue gases are directed into a heat exchanger, where they are heated to the appropriate temperature and then released through a chimney into the atmosphere. The reagent of the flue gas cleaning process - seawater - is directed to the top of the absorption vessel, where it is sprayed onto the flue gases. In doing so, a reaction takes place that separates sulphur dioxide [SO_2] and hydrochloric acid [HCl] from the flue gases. Part or all of the reagent used in the purification process may be the cooling water originating from the condenser

in the Clausius-Rankin cycle. When the reagent reaches the bottom of the absorption vessel, it is retained and then pumped into the spent reagent handling pool before being released back into the sea. When the flue gases come into contact with seawater inside the absorption vessel, the sulphur dioxide compound begins to dissolve and bisulfide is formed. Part of the resulting bisulfide can then be converted to sulphite. This reaction occurs in the two chemical reactions described below:



Oxygen is found both in the flow of flue gases and in the seawater. Due to the presence of this oxygen, the resulting bisulfide and sulphite from the above two equations are oxidised to sulphate through the following two chemical reactions:



In the process of decomposition of sulphur dioxide in seawater to form bisulfide and sulphite (and consequently sulphate), positively charged hydrogen ions are also formed. These positively charged hydrogen ions oxidise the seawater in the reaction vessel and lower its pH. Thus, acidified seawater must be properly neutralised to maintain the appropriate conditions for the existence and preservation of ecosystems and organisms in seawater. Neutralisation of previously used seawater inside the absorption vessel is achieved with compounds that form an integral part of seawater. The chemical reactions describing the neutralisation of acidified seawater are as follows:



To achieve the appropriate alkalinity, the neutralisation process takes place in the first zone of the collection basin, where fresh seawater from the cooling system of the thermal power plant is added to the oxidised seawater. The medium in the first part of the collection basin must be thoroughly mixed before entering the next zone. A further part of the collection basin is the zone where the air is blown into the well-mixed seawater medium. Blowing air and thoroughly mixing the effluent from the SWFGD process constitutes an important step from an ecological and technical point of view if we want to ensure the effective operation of the treatment process. [7] By optimally blowing air into the pool, we achieve:

- Optimal and satisfactory oxidation and compounds;
- Adequate efficiency of neutralisation of the medium before its discharge into the sea;
- The restoration of adequate oxygen concentrations in seawater.

4 SEAWATER AS THE PROCESS REAGENT

Seawater used as a reagent in the flue gas cleaning process is subject to certain requirements before being discharged back into the sea. The following are particularly important:

- When the process seawater is taken from the sea itself, the pH value of the seawater returned from the process back to the sea must be as close as possible to the original pH value;
- The temperature of the seawater being returned to the sea must not significantly exceed the average seawater temperature before its initial removal from the sea;
- The COD (Chemical Oxygen Demand) value must be as low as possible;
- The value of dissolved oxygen must be suitably high;
- The level of sulphates in the seawater being returned to the sea must be as low as possible;
- The concentration of particulate matter in the seawater being returned to the sea must be correspondingly low.

Upon the discharge of the absorption vessel, once the flue gas cleaning has been completed, the pH value of the reagent – seawater - is about 3 to 4. Since the critical value for the acidity of seawater for marine and marine organisms is about 6.5, acidified seawater must be de-acidified before its discharge into the sea. The basicity of seawater is increased through the aforementioned process of blowing air into the seawater before releasing it back into the sea. At the outlet from the pool, where the air is forced into the used seawater, the pH value is controlled, which must be between 6 and 7. When seawater returns from this process, it is about 2 °C warmer prior to its discharge into the sea compared to when it was initially taken from the sea. The amount of dissolved oxygen in seawater capture before entering the process is between 50% and 100%, while at the outlet, following its treatment in the mixing basin and after the forced air blowing process, the proportion of dissolved oxygen in seawater is closer to 70% to 90%, or more than 6 mg/L. Near thermal power plants using the seawater desulphurisation process, long-term seawater wastewater quality monitoring has not demonstrated any adverse effects on the ecosystem, the marine environment, or on the animals. The so-called COD (Chemical Oxygen Demand) method is also used to determine the quality or pollution of seawater at the outlet of the mixing and ventilation basin. This is the standard method for indirectly determining the degree of contamination of an aqueous sample. This method is based on the chemical decomposition of organic and inorganic compounds and elements in an aqueous sample. The result of this method gives us the equivalent of the amount of water - dissolved oxygen in the aqueous sample (given in ppm) or in mg/L, which is used for its decomposition by water pollutants during a two-hour decomposition process in boiling potassium dichromate. In the case of a smaller industrial plant with an SWFGD plant, the permitted number of COD in the discharged seawater is approximately 100 - 150 mg/L. If the SWFGD plant is upgraded to a larger thermal power plant (700 MWe and more), where the flow of consumed seawater as a reagent through the flue gas cleaning system can exceed 100,000 m³/h, which is equivalent to the flow of a smaller river, the COD limit is 5 mg/L.

Table 1: Typical chemical elements & compounds within seawater

Element	Quantity	Unit
Cl^-	19.35	[g/kg]
Na^+	10.76	[g/kg]
SO_4^{2-}	2.71	[g/kg]
Mg^{2+}	1.29	[g/kg]
Ca^{2+}	0.41	[g/kg]
K^+	0.40	[g/kg]
HCO_3^-	0.14	[g/kg]

Dissolved oxygen in water allows the oxidation of sulphite to sulphate. The rate of this reaction is influenced by the pH value of the seawater. The most efficient flue gas cleaning procedure inside the absorption vessel should be at a pH value of seawater between 4.1 and 4.5 and between 5 and 5.6. Most of this oxidation takes place inside the absorption vessel. However, for complete oxidation, it is necessary to forcibly blow oxygen into the sea-wastewater treatment pool. With the SWFGD plant, it is possible to achieve high efficiency of sulphur extraction from the flue gas stream in thermal power plants (> 99%), but it is also necessary to ensure that the COD value (Chemical Oxygen Demand) is between 2.5 and 5.0 mg/L. The oxidation process continues even after the discharge of processed seawater back into the sea, and so it is important to ensure an adequate level of oxygen upon the discharge of the medium into the sea. [8] The amount of oxygen in the processed water discharged into the sea during the SWFGD process is regulated by Council Directive 79/923/EEC. In Table 2, the discharged seawater quality parameters of a typical SWFGD process are presented.

Parameter	Unit	Inlet seawater	Discharge
pH	/	8.2	6 - 7
COD	mg/L O ₂	0	2.5 - 5.0
DO	%	50 - 100	70 - 90
Sulphate	mg/l	2700	2785
Temperature	°C	T	T + 1,5
Salinity	%	33.5	33.5
Suspended solids	mg/L	SS	SS + 1

The following section describes and discusses the degree of impact stemming from the main factors that may provoke environmental concerns, as well as their potential consequences on relevant organisms. The rise of temperature in seawater, where effluent water is returned to the sea, occur in small area where temperature is elevated in duration less than 1 minute. Therefore, we can assume that any rise in the water's temperature will have an insignificant

impact on the environment, the quality of the seawater, and the species residing in it across the broader observed area. However, the rise in local sea temperature at the moment of discharge of the effluent water back into the sea represents the primary factor of mortality for the pelagic organisms (see Table 3). The pH – pH of effluent water returned to the sea can have a pH between 6 to 7. Pelagic organisms are exposed to this pH for a period of 15 minutes, depending on the average current velocity. This time exposure to pH in the range of 6 – 7 should not cause any significant effect on pelagic organisms. Benthic organisms will also not experience any adverse effects, since the effluent water from the SWFGD process is returned to the sea and dispersed in the upper layers of the seawater.

Chemical Oxygen Demand and dissolved oxygen – the expected values of both parameters are presented in Table 2. Organisms can be affected by a deficit of dissolved oxygen within 250 m from the discharge of effluent water from the SWFGD process. The direct exposure to dissolved oxygen deficit is evaluated for 15 minutes. Salinity – in the case of seawater evaporation in cooling towers and scrubbers, the 12% increase in the concentration of Na⁺ ions can be expected in the effluent water entering the collection pit and aeration channel. Many of the pelagic organisms can adapt to variation in the salinity of the seawater in the range of $\pm 18\%$. Therefore, the possible change in salinity concentration should not have a direct impact on pelagic organisms. Sulphate – ambient seawater contains an amount of SO₄ in the range of 3200 – 3650 mg/L, depending on the amount of salinity concentration in the local seawater. As stated in the description of salinity change, a variation in sulphate concentration is also acceptable for the pelagic and benthic organisms within the range of $\pm 18\%$. Suspended solids – the desulphurisation process using seawater as a reagent produces an additional amount of suspended solids in the effluent water returned to the sea within a range of less than 1mg/L.

Table 3: Survival possibility of species in nearby seawater where SWFGD scrubber effluent is discharged back to the sea*

Species	Effluent concentration	Seawater temperature
Milkfish larvae	□	■
Milkfish juveniles	□	□
Copepods	□	□
Clams	□	□
Eel elvers	□	□
Black seabreams	■	□
Tiger prawns	□	□

*Legend: □ – not affected; ■ - affected

None of the aforementioned environmental impacts originating from the SWFGD process are severely harmful to the environment, nor the species that reside within it. We can thus conclude that seawater, when used as the medium in the scrubbing process of raw flue gas flow in the SWFGD process, is a good medium for scrubbing sulphur components in raw flue gases before they enter our atmosphere. [9] Seawater is especially appropriate to be used as a reagent since it has an inherited alkalinity concentration of approximately 100 – 110 mg/L of CaCO₃.

At the same time, it is important to point out that seawater already has an existing amount of sulphur in it, approximately 0.9 kg of sulphur per 1 tonne of seawater. [10]

5 CONSTRUCTION MATERIALS

The choice of construction materials is crucial to ensure a suitably long service life and to safeguard the initial investment amount of the flue gas treatment plant. High corrosion in flue gas desulphurisation plants can be caused by both the flue gases originating from the steam boiler and the oxidised seawater that is retained in the absorption vessel. The use of Hastelloy® and Duplex stainless steel is very expensive and can greatly increase the initial investment in an SWFGD treatment plant. To optimise investment costs, other construction materials can also be used, such as FRP (Fibre Reinforced Polymer), chlorine-butyl rubber, silicone rubber, etc. It is also possible to use ordinary structural steels, which are wall-coated with stainless steel. It is crucial to foresee the proper material choice for key process equipment. Only by doing this can the long-lasting and reliable operation of flue gas desulphurisation plants be achieved. The main absorber vessel and pumps with corresponding pipelines constitute key pieces of equipment.

6 COST COMPARISON OF ABATEMENT TECHNOLOGIES

The following technologies for cleaning flue gases in a big thermal power plant in terms of removing sulphur dioxide from raw flue gases are different in their operating principles as well as in initial investment and, later, their operational costs.

Table 4: Cost comparison for the flue gas desulphurisation process using different available abatement technologies

DESULPHURISATION OF FLUE GASES					
	Load Factor [%]	Emission Rate [mg/Nm ³]	BREF limit [mg/Nm ³]	Capital cost [€/MW]	Cost per unit power generation [€/MWh]
WET FGD	30	< 100	150-175	300.000,00	7,00 €
	70	< 100	150-175	300.000,00	5,99 €
WET FGD UPGRADE	30	100	130-320	22.500,00	2,13 €
	70	100	130-320	22.500,00	3,90 €
SEMI DRY FGD	30	100-500	130-320	90.000,00	3,62 €
	70	100-500	130-320	90.000,00	5,11 €
DRY FGD	30	50-200	130-320	110.000,00	3,37 €
	70	50-200	130-320	110.000,00	3,88 €
SWFGD	30	< 200	130-320	70.000,00	0,83 €
	70	< 200	130-320	70.000,00	1,98 €

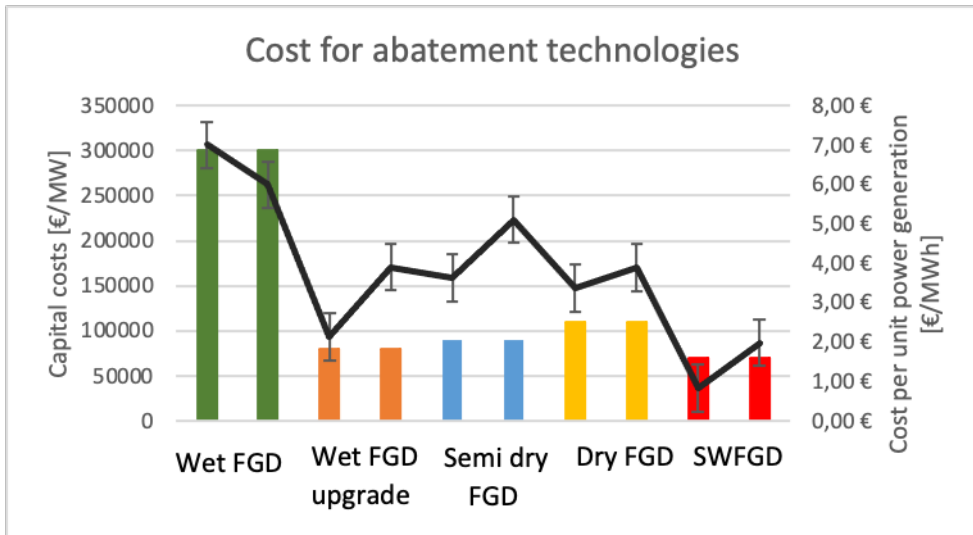


Figure 3: Cost of abatement technologies

The new BREF directive is going to limit the emission rates for big thermal power plants as shown in table 2. Depending on the steam boiler load factor, the new BREF limits will need to be met. In the case of the new wet FGD system, the new regulative proposes emission limits between 150 – 175 mg/Nm³. In the case of upgrading the existing wet FGD system, the emission limits propose the emissions in the range between 130 – 320 mg/Nm³. The same emissions level range is predicted for the semi-dry and dry process of flue gas desulphurisation processes as well as for the SWFGD. [11]

7 CONCLUSION

Since the SWFGD process necessitates access to fresh seawater, it is locally limited to coastal areas. This same flue gas cleaning process can also be used in the use or incineration of coal with a high sulphur content, but consideration must be given to the fact that high concentrations of sulphur dioxide in the flue gases would require an additional amount of seawater in the process to achieve adequate efficiency. This additional required amount of seawater cannot be provided only from the cooling system of the thermal power plant, and so it is necessary to provide additional captures of seawater directly from the sea, something which increases the investment and operating costs of flue gas treatment plants. The main advantages of the SWFGD process are as follows:

- SWFGD does not typically require any chemical reagents for its operation;
- During the process of operation of the treatment plant, no by-products are created that could be dangerous for the environment and living beings;
- The design of the plant is simple. This enables the plant's reliable operation and long service life, assuming that the appropriate construction materials were selected during its construction;

- The process allows up to 99% removal of sulphur dioxide from flue gases.

For adequate economic profitability of the SWFGD process, we envisage the use of fuel - coal, with a sulphur content of up to 1.5%. If coal with a higher sulphur content is burned in a thermal power or industrial plant, then the additional use of sorbents is required within the SWFGD flue gas cleaning system. These sorbents can be limestone, sodium hydroxide, or magnesium oxide. The use of such sorbents is sometimes necessary to achieve adequate removal of sulphur dioxide from the flue gases in the absorption vessel and to neutralise seawater waste before it is discharged from the process and is returned back to the sea.

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Nomenclature

(Symbols)	(Symbol meaning)
LFSO	Limestone Forced Oxidation System
MEL	Magnesium Enhanced Limestone
SWFGD	Sea Water Flue Gas Desulphurisation
SO₂	Sulphur Dioxide
U.S.	United States
FGD	Flue Gas Desulphurisation
HCl	Hydrogen Chloride
COD	Chemical Oxygen Demand