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ABSORPTION OF FLUE GASES IN SEAWATER

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ABSTRACT

Existing and proposed technologies for absorbing flue gases into seawater are reviewed. Seawater scrubbing has been employed in industrial plants to desulphurise flue gases by means of conventional absorbers for several decades. More recently, it has been suggested that flue gases may be piped directly to the sea obviating the need for an absorption tower and chimney stack. Almost complete absorption of sulphur dioxide may be achieved by bubbling flue gases into the surface ocean, while effective removal of carbon dioxide requires disposal at considerable depth. Short-circuiting the environmental cycle by direct disposal of these pollutants into the oceans is an elegant geochemical solutions to many of the problems of air pollution.

KEYWORDS

Air pollution, Desulphurisation, Seawater, Carbon dioxide, Sulphur dioxide

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INTRODUCTION

Fossil fuel combustion, refining of petroleum, smelting of ores and other industrial processes release huge quantities of pollutants into the atmosphere. Considerable concern has been expressed about two major industrial pollutants, sulphur dioxide (SO₂) and carbon dioxide (CO₂) which contribute to acid rain and global warming, respectively. The multifarious consequences of this pollution include: damage to human and animal health, acidification of lakes and rivers and death of fish, damage to forests, and changes in weather and climate. While emissions of these pollutants are expected to decrease in Western Europe and the U.S. over the next 20 years, emissions in developing countries, especially in Asia, are predicted to increase significantly [1].

The abatement of global air pollution problems such as acid rain and global warming is high on the political agendas of national governments and international organisations. Consequently, there is a growing demand for practical and cost-effective air pollution control technologies which could be applied to a wide range of industrial plants, especially in developing countries. One important but not widely recognised method, that has been in use for half a century, is absorption of flue gases into seawater [2]. This method has been used to desulphurise flue gases and it is based on the high solubility of SO_2 in seawater. Recent research suggests that further improvements, which could extend the efficiency and applicability of this technology, are possible.

Absorption of flue gases into seawater can be effected in one of two ways:

- (i) By means of a conventional absorption tower (either spray or packed). This technology is well established and all past and present industrial applications of the seawater scrubbing method are based on it [3].
- (ii) By means of direct disposal of flue gases into the sea. This method, which obviates the need for an absorption tower and a chimney stack, has yet to be tried in practice [4].

Control of the two most important flue gases, SO_2 and CO_2 , by means of absorption into seawater will be discussed in the present paper. Theoretical principles, industrial applications, laboratory studies, environmental consequences, and proposed future technologies are reviewed.

INDUSTRIAL PLANTS

Flue gas desulphurisation (FGD) at industrial plants has been achieved by contacting flue gases with seawater, or other reagents (e.g. lime/limestone), inside conventional absorption towers. One of the earliest applications of FGD was at Battersea power station in London where a desulphurisation plant employing Thames estuarine water with added chalk was built in the 1930s and it achieved SO₂ absorption efficiencies of *ca.* 90% [5]. In the 1940s the Electrolytic Zinc Company in Tasmania used tidal estuarine water to desulphurise smelter flue gases containing *ca.* 3 % SO₂ with an efficiency of 99.9% [6]. In the 1960s, seawater was employed to desulphurise boiler flue gases at the Showa Denko Company in Yokohama, Japan [7]. In the 1970s,

three different FGD systems based on seawater scrubbing were patented in Japan [8,9,10]. One of these, involving electrolysed seawater, removed SO_2 with an efficiency of 99.9% [10]. Another involved spraying the flue gas with seawater containing CaCO₃, with or without CaSO₄, to obtain gypsum [9].

Flue gas desulphurisation efficiencies greater than 99% have been reported for many of the seawater based scrubbers demonstrating the effectiveness of the process [3]. Some of these claims may be somewhat exaggerated as they are based on a limited number of tests under ideal conditions. Nevertheless, high efficiencies of around 90-95% may be routinely obtained in practice. The efficiency depends on the liquid/gas (*L/G*) ratio and higher efficiencies may be easily achieved by increasing this ratio, albeit at a higher cost.

Today, the largest supplier of seawater based FGD absorbers is Alstom who market the seawater FGD system previously known as the Fläkt-Hydro process involving counter-current absorption of flue gases into seawater. This process has been applied at many coastal and island industrial sites across the world, including oil and coal fired boilers, smelters, refineries and incinerators. Fläkt-Hydro seawater based scrubbers operate in Scandinavia, India, Indonesia, Canary Islands, Malaysia and the U.S. (island of Guam) and numerous seawater FGD plants are currently being built or in the planning stage in China. A process involving seawater with lime additive has been developed by Bechtel [11,12].

A flow diagram of a typical seawater scrubbing plant is shown in Fig. 1. Seawater is passed through a screen in order to remove fish, weeds and other suspended materials before being pumped to the top of the scrubbing tower. The seawater is sprayed inside the tower where it reacts with the counter-flowing flue gas. The flue gas is introduced at the bottom of the tower after passing through a dust collection device (e.g. cyclone) in order to remove harmful particulate matter which may be collected by the scrubbing solution and discharged to the sea. After passing through the scrubbing tower the purified gas flows through a reheater before being discharged to the atmosphere via the chimney stack. The reheating of the gas increases plume buoyancy and assists dispersion. The gas can also be passed through a demister to remove any entrained droplets. The spent seawater flows from the bottom of the tower into a water treatment plant. Water treatment may involve dilution with further seawater from the condensers, aeration and/or liming. In addition to expelling absorbed CO₂ (if this is deemed desirable) to raise the pH and assist SO₂ oxidation, aeration also raises the O₂ content of the effluent to levels suitable for disposal to the sea. The effluent seawater may be diluted with seawater from power station condensers before discharge. In some seawater based desulphurisation plants no water treatment is employed. Either spray or packed absorbers can be used, and it is also possible to operate these either on a once-through basis or with seawater recirculation.

GAS/LIQUID EQUILIBRIUM

In the absorption tower, gaseous pollutants are transferred from a bulk gaseous phase into seawater droplets or films. Sulphur dioxide absorption involves Henry's Law equilibrium followed by rapid dissociation to bisulphite and sulphite ions:

$$H \longrightarrow SO_2 + H_2O \longrightarrow SO_2 H_2O$$
 (1)

$$SO_2 H_2O \longrightarrow HSO_3 + H^+$$
 (2)

$$HSO_{3}^{-} \xrightarrow{K_{2}} SO_{3}^{2-} + H^{+}$$
(3)

where H is Henry's Law constant, and K_1 and K_2 are the first and second dissociation constants respectively, and these are defined in terms of the activities of the various species. The total concentration of dissolved S(IV) may be related to the gaseous partial pressure of SO₂ using a pseudo-Henry's Law constant defined as:

$$H^* = H\{1 + K_1/a_{H^+} + K_1K_2/(a_{H^+})^2\}$$
(4)

where a_{H+} is the activity of the hydrogen ion. Same equilibria apply to CO₂ dissolution except that physically dissolved CO₂ (CO₂·H₂O), bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) replace physically dissolved SO₂, bisulphite and sulphite respectively in equations 1-3. Equilibrium constants for SO₂ and CO₂ are summarised in Table 1.

The efficiency of absorption, assuming complete equilibration, may be calculated from [13,14]:

$$E(\%) = (L/G) R T - 100$$
(5)
(L/G) R T + 1/H*

where L/G is the volumetric liquid to gas ratio, R is the gas constant (0.082 L atm mol⁻¹ K⁻¹) and *T* is the absolute temperature.

Dissolved SO₂ is rapidly oxidised to sulphate in seawater:

$$SO_3^{2-} + \frac{1}{2}O_2 \longrightarrow SO_4^{2-}$$
 (6)

The reaction involves oxidation by O_2 which is significantly enhanced by the high level of chloride present in seawater [15,16]. Both the solubility of SO_2 and the rate of oxidation increase with increasing pH. On the other hand, CO_2 dissolved in seawater is present predominantly in the form of bicarbonate ion, and absorbed CO_2 may be desorbed if the solution becomes acidic.

The absorption efficiency is illustrated as a function of the *L/G* ratio and pH in Fig. 2. Almost complete absorption of SO₂ can be achieved at relatively low *L/G* ratios over much of the pH range. The efficiency of SO₂ absorption only begins to drop off significantly at pHs < 4. On the other hand, the absorption efficiency of CO₂ decreases sharply between pH of 8 and 5, remaining constant at pH<5. Much higher *L/G* ratios are needed to obtain modest absorption efficiencies of CO₂. Higher absorption efficiencies of gases could also be achieved by adding alkaline substances such as caustic soda (NaOH) to the seawater scrubbing solution to raise the pH.

Absorption and oxidation of SO_2 in seawater will lower the pH and limit the further uptake of SO_2 , the solubility of which decreases with increasing acidity. The decrease in pH is, however, much less pronounced in seawater than in pure water due to the buffering capacity of seawater. The pH of the liquid effluent from a seawater scrubbing plant depends on the *L/G* ratio and the concentration of SO_2 in the flue gas. Higher *L/G* ratios would result in high pH and the effluent could be discharged to the sea without further treatment. Low *L/G* ratios would result in an acidic effluent which may require dilution with cooling water from condensers or addition of lime prior to discharge.

Theoretical calculations predict extremely high desulphurisation efficiencies (>99%) at *L/G* ratios typical of operating scrubbers, in agreement with measurements in actual industrial applications. Although some absorption of CO_2 is predicted by calculations, and is observed in practice [17], the process is reversible, in contrast to SO_2 absorption which rapidly leads to the formation of stable sulphate ions [15,16,18]. Any absorbed CO_2 may be desorbed if the solution becomes acidic. The solubility of CO_2 is much lower than that of SO_2 , and at corresponding *L/G* ratios the absorption efficiency for CO_2 is considerably lower than for SO_2 .

Other flue gases may also be controlled by absorption into seawater. Hydrogen chloride gas, with a Henry's law constant of 20 mol L⁻¹ atm⁻¹, is extremely soluble in water and it will readily dissociate to chloride ions. The Henry's law constant for H₂S is 0.1 mol L⁻¹ atm⁻¹, intermediate between that of CO₂ and SO₂, and it too may be absorbed in seawater. On the other hand, oxides of nitrogen are relatively insoluble and seawater scrubbing cannot be used to reduce NO or NO₂ to any significant extent, as confirmed by laboratory experiments [17]. However, the seawater method may be combined with a method of NO_x removal from flue gases such as selective

catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) to achieve combined reduction of SO_2 and NO_x [19].

LABORATORY STUDIES

There have been very few laboratory studies of SO_2 - seawater interactions and these are summarised in Table 2. Only two of these studies are relevant to the conditions encountered in flue gases; one employed a bench-top scrubber while the other employed a bubbler. These experimental studies confirm theoretical predictions and plant measurements. Studies involving bubblers report 100% absorption of SO_2 [18], some absoption of CO_2 , and very low absorption of NO [17].

The buffering capacity of seawater has also been investigated in laboratory experiments [17,18]. These studies show that seawater can accommodate significant quantities of acid without a significant change in pH. The buffering capacity begins to break down at around 10^{-3} mol I^{-1} H⁺ and at 10^{-2} mol I^{-1} H⁺ any advantage of using seawater over pure water is lost (Fig. 3).

DIRECT DISPOSAL TO THE SEA

Surface Ocean

Theoretical, laboratory and plant studies all show that the efficiency of desulphurisation is a function of the L/G ratio. The contact times in conventional scrubbers are brief, of the order of seconds. This is too short for complete equilibration but, nevertheless, very high desulphurisation efficiencies can be achieved with conventional scrubbers for most applications. For very large power plants it may be difficult to achieve the high L/G ratios using conventional scrubbers. Laboratory studies have shown that 100 % absorption of SO₂ may be achieved simply by bubbling the gas into seawater [17,18]. Much higher L/G ratios and longer contact times could be achieved if the flue gases could be piped to the sea and bubbled under the surface. Whereas in conventional absorption towers mass transfer is from a bulk gaseous phase into droplets or films of seawater, in this novel method mass transfer is from bubbles of gas into bulk seawater liquid phase. This method obviates the need for an absorption tower and chimney stack [4].

An illustration of a hypothetical direct discharge system is shown in Fig. 4. Flue gas is first passed through a dust collection device (e.g. electrostatic precipitator). A compressor is required to overcome the pressure of water; for each 10 meters of depth one atmosphere of pressure must be overcome. Hydrogen chloride, sulphur dioxide and carbon dioxide in the flue gas will dissolve to give soluble chloride, sulphate and bicarbonate ions. While the method would give quantitative absorption of HCI and SO₂, the absorption efficiency of CO_2 in the surface ocean would be considerably lower, and volatilisation of CO_2 may occur. It may also be possible to mix air in with the flue gas in order to maintain high dissolved oxygen levels and increase the rate of oxidation of SO₂ to sulphate. Also, the flue gases may be passed

through a NO_x reduction unit (e.g. SCR or SNCR) [19] in order to reduce oxides of nitrogen, before being bubbled underwater. It may be necessary to cool the flue gas prior to discharge since high temperatures can have negative impacts on marine ecosystems. Decreasing the flue gas temperature will also increase the absorption efficiency as the solubility of gases increases with decreasing temperature.

Deep Sea Injection

Because of the low solubility of CO_2 in the surface ocean, disposal and storage of CO_2 in the deep ocean has been proposed by a number of workers as a possible solution. Although a number of different schemes have been proposed in the literature these are all hypothetical and have not been tested or tried in practice. Some are just speculative proposals not backed up with hard data while others are based on models of varying degrees of complexity. Table 3 summarises the various proposals for oceanic disposal of CO_2 . As there are still some uncertainties in our knowledge of the fate of CO_2 in the oceans [20, 21] these proposals remain to be substantiated.

The proposed methods may be broadly classified into three categories:

- (i) Direct bubbling of flue gas at great depth (e.g. 240 m).
- (ii) Absorption of CO₂ into seawater followed by pumping of the effluent from the scrubbing plant into the ocean. Due to the higher density of the CO₂containing seawater from the plant than the surrounding seawater, the CO₂-containing seawater would sink to the bottom of the ocean.
- (iii) Absorption of CO_2 into a scrubbing solution (e.g. monoethanolamine) in an absorber followed by recovery of the CO_2 and its injection into the sea.

Most of the proposed methods involve recovery of CO_2 from the flue gas followed by injection into the sea. Carbon dioxide from the flue gas is first absorbed into a solution inside an absorption tower. Chemical absorbers which have been considered include aqueous solutions of alkalis (KOH, NaOH), salts (K₂CO₃, Na₂CO₃, K₃PO₄) and amines (mono-, di-, and tri-ethanolamine). In the case of monoethanolamine solution the following reaction can be used to illustrate the absorption process:

 $C_2H_4OHNH_2 + H_2O + CO_2 \longrightarrow C_2H_4OHNH_3^+ + HCO_3^-$ (7)

The forward reaction is favoured at lower temperatures whereas high temperatures favour the reverse reaction. Thereafter, the absorbed CO_2 is released inside a stripper at high temperature (100-120 °C) and the absorbing solution is recycled back to the absorption tower. Other methods for the recovery of CO_2 from the flue gas that have been suggested include cryogenic fractionation and membrane separation [22]. It is proposed that the recovered CO_2 be compressed and transported by pipeline to the sea. Varying depths of injection have been proposed. In one proposal it is suggested that the CO_2 can be injected into sinking thermohaline currents at a depth

of 160m. These currents then carry the CO_2 to the bottom of the oceans where, it is claimed, it may remain for up to 500 years [23,24]. In other proposals it is suggested that CO_2 should be injected at greater depths of up to 3000 m [25]. The recovered CO_2 could be injected into the deep ocean as gas, liquid or solid (dry ice).

A method involving the absorption of CO_2 in seawater in a pressurised pipeline followed by injection of this seawater into the ocean at depths of 200 to 400 m has been patented by Mitsubishi [26]. Since the seawater containing dissolved CO_2 has a higher density than ordinary seawater it is expected to sink to the bottom of the ocean where it will accumulate as carbon dioxide hydrate. A similar method has been proposed by Haugan and Drange [27].

Some of these methods have been assessed in terms of their potential cost, and these tend to be prohibitive. It is unlikely that deep sea injection will be practiced in the near future as between 30 and 45% of the power produced by the power station would be used for operating the CO_2 disposal method. One proposed method would even require more energy than could be produced by the power station [28]. Another rather eccentric proposal even suggests the building of floating power stations [25].

The main controversy and point of dispute with these proposed methods seems to be the fate of the disposed CO_2 in the oceans. In one study, it was suggested that CO_2 so disposed would remain permanently at the bottom of the oceans due to the density of liquid or solid CO_2 being greater than that of the overlying seawater [25]. De Baar and Stoll [20] have critically assessed the various proposals for the deep sea disposal of CO_2 and concluded that the fix is not permanent; the CO_2 would slowly diffuse into the surface ocean and eventually into the atmosphere. They conclude that deep ocean disposal would lead to a delay of several hundred years; for most proposed methods half of the injected CO_2 would be released to the atmosphere within 50 to 500 years.

ENVIRONMENTAL IMPACTS

Seawater is a suitable recipient for pollutants such as SO₂, CO₂ and HCl which are produced mainly by the combustion of fossil fuels. These gases are converted to sulphate, bicarbonate and chloride ions in seawater and these very ions are major constituents of seawater (Table 4). Seawater is a concentrated electrolyte solution containing 18.97 g Cl⁻, 2.56 g SO₄²⁻ and 0.14 g HCO₃⁻ per kg. Furthermore, seawater has a considerable buffering capacity and can resist changes in its pH upon addition of acids. Addition of these ions from flue gases is unlikely to have adverse effects on marine ecosystems which are already adapted to this chemical environment. Minor components in the flue gas such as heavy metals should not pose a problem since these can be minimised by passing the flue gas through a dust control device prior to discharge to the sea. Detailed long-term studies near the outfall from a seawater based desulphurisation plant have not revealed any damage on the local marine ecosystem [29]. Although absorption of flue gases into seawater essentially converts air pollution into water pollution, the effluent from a seawater based desulphurisation

plant can meet even the most stringent environmental standards such as those in Scandinavia and the European Union as shown by successful operation of plants in Scandinavia and the Canary Islands.

As mentioned previously, seawater exhibits a buffering capacity and can withstand changes to its pH upon addition of acidic or alkaline substances, unlike fresh waters which suffer markedly upon addition of small quantities of acidic substances in the form of acid rain. The buffering action of seawater is due to the high bicarbonate concentration. Absorption of acidic substances may displace some CO_2 out of solution in order to maintain the pH:

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$
 (8)

Hence, while controlling one problem, acid rain, the process may be contributing to another, global warming. However, the picture is not so simple as other processes such as those involving borate, calcite and clay minerals can also act to buffer the acidity. In the long term, the seawater pH is controlled by the so-called "pH-stat" mechanism in which H^+ ions in solution exchange with Na⁺ ions in clay sediments [30].

A simple calculation demonstrates that if for the next 100 years all the industrial emissions are absorbed into seawater, the background concentration of sulphate in seawater would increase by less than 10^{-3} %, a negligible quantity. Assuming a present day seawater pH of 8, the pH of seawater after 100 years would remain virtually unchanged. This negligible effect is due to the buffering capacity of seawater. If seawater had no buffering capacity the resulting pH would be 6.5. This calculation assumes a mixing time of 100 years for the oceans, which may be unrealistic due to the slow mixing between the surface and deep ocean. It is estimated that water in the oceans is turned over completely in several hundred years [31]. Nevertheless, this calculation illustrates the ability of the oceans to take up SO₂ pollution.

With regard to the deep sea injection of CO_2 , the environmental consequences are unknown as the method has not been tested in practice. One theoretical assessment suggests unfavourable consequences on marine ecosystems [20].

CONCLUSIONS AND RECOMMENDATIONS

Seawater scrubbing has been employed successfully for several decades to control industrial emissions of SO_2 without any harmful effects on marine ecosystems. Unlike many other processes of FGD (e.g. lime/limestone method), seawater scrubbing creates no solid waste products. Seawater scrubbing is a reliable and simple method with low capital and operating costs, however, its use is restricted to coastal locations. Despite these successes, seawater scrubbing still commands a minor share of the FGD market; one possible reason may be that this little known method has been poorly publicised. Very few reviews of FGD technology mention the

seawater method. Desulphurisation technology is dominated by lime and limestone methods which control ca. 90% of the world market in FGD technology. The advantages of seawater scrubbing are apparent from Table 5 in which the seawater is compared with the currently popular lime/limestone method method. Lime/limestone methods rarely achieve efficiencies greater than 90% and problems due to plugging of scrubbers by limestone slurries are not uncommon, although there have been some recent improvements in this technology. These methods involve the quarrying and transporting of limestone to the plants, preparing the slurry, and disposing of spent slurry. Although all of these steps entail economic costs, the highest cost of the lime/limestone method is environmental; limestone guarries are not only eyesores, but are also a growing threat to our shrinking green belts. On the other hand, seawater scrubbing is a simple, efficient, and inexpensive FGD method with no significant impacts on the environment. Seawater scrubbers could meet the growing demand for practical and cost-effective air pollution control technologies. especially in developing countries. Island nations, and those with access to the sea could find this technology most suitable, as shown by applications in the Canary Islands and Indonesia.

Sulphur dioxide is effectively absorbed into seawater in conventional scrubbers, although direct disposal to the sea would further simplify the process and improve the absorption efficiency. The oceans are the final recipient of water soluble air pollutants even when these are discharged into the atmosphere. These pollutants are eventually transported to the oceans through the hydrological cycle damaging weakly buffered lakes, rivers and soils on the way as well as impacting on materials. Discharging these gases into the oceans represents an elegant geochemical solution to the problems of air pollution, preventing pollutants from entering the atmosphere in the first place. Bubbling flue gases directly into the sea represents a novel and highly effective approach to air pollution control but it still remains to be tested in practice. It appears that effective removal of CO_2 may require deep sea disposal. Although several methods for the injection of CO_2 into the oceans have been proposed, none has yet been tried. It is unlikely that deep sea injection will be practiced in the near future as a large fraction of the power produced by the power station would go into operating the CO_2 disposal method.

Methods involving the disposal of flue gases into the ocean are examples of "biogeochemical engineering" in which natural biogeochemical processes are utilised to solve environmental problems. This represents a novel approach to environmental management.

Future studies should concentrate on field trials of the direct injection of flue gases into the sea as well as finding new applications for the method. Field trials have not yet been carried out and pilot plant studies are urgently required in order to optimise operating parameters (depth of discharge, diffuser type, etc.) and resolve some of the uncertainties regarding the fate of dissolved gases in the ocean. Demonstration of this novel method in practice would greatly benefit the power generation industry since it would demonstrate that fossil fuels can be burnt in an environmentally acceptable manner. Furthermore, this technology could be applied to shipping. As emissions from stationary and vehicular sources of SO_2 and NO_x continue to decrease in many regions of the world, due to the introduction of more stringent legislation and the application of SO_2 and NO_x reduction technologies to stationary sources and the introduction of catalytic converters in motor vehicles, the contribution of shipping to the atmospheric emissions of these gases will increase. Shipping is increasingly being recognised as a source of air pollution, and legislation is being planned to control emissions from marine sources. Seawater based FGD methods could be conveniently applied to these sources.

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SO ₂	CO ₂
1.242	0.031
0.0132	4.3x10 ⁻⁷
6.24x10 ⁻⁸	5.61x10 ⁻¹¹
1.19x10 ⁷	1.371
	1.242 0.0132 6.24x10 ⁻⁸

Table 1. Values of equilibrium constants for SO₂ and CO₂ at 25 $^{\circ}$ C.

H* is for pH 8.

Study/reference	Type of study	SO ₂ concentration (ppmv)	Comments
Spedding [32]	Air containing SO ₂ passed over seawater	0.003 - 1.3	Low concentrations not relevant to flue gases
Bromley [33]	SO ₂ in air absorbed in 6- inch by 10-foot spray and packed tower	890	Absorption efficiency increased with increasing liquid/ gas ratio. Betweer 88.5 and >99.9% of the SO ₂ could be absorbed
Clarke & Radojevic [16]	Oxidation of sulphite in seawater	Dissolved S(IV) concentrations between 10 ⁻⁵ and 10 ⁻⁴ mol L ⁻¹	Low concentrations not relevant to flue gases. Evaluated kinetic constants.
Radojevic & Tressider [17]	Air containing SO ₂ bubbled through seawater	4000 ppmv	Complete absorption of SO ₂ . Also studied buffer capacity of seawater.

Table 2. Experimental studies of SO₂-seawater interactions

Reference	Method	Injection depth	CO ₂ recovery	Scrubbing solution	Comments
Marchetti [23,24]	SSCIª	NR^{d}	50%	K ₂ CO ₃	Injection into sinking thermohaline currents
Mustacchi et al [34]	DIFG⁵	240 m	95%	-	Cost: 43% of total power produced
Mustacchi et al [34]	SSCI	160 m	95%	Various absorbents	Cost: 20% of total power produced
Mustacchi et al [34]	SI ^c	10 m	NR	Seawater	Cost: 20% of total power produced
Baes et al [25]	SSCI	1000 m	90%	Various absorbents/ Seawater	Absorption of purified CO ₂ into seawater followed by deep sea injection of concentrated seawater solution.
Baes et al [25]	SSCI	3000 m	90%	Various absorbents	Injection of liquid CO ₂
Baes et al [25]	SSCI	500 m	90%	Various absorbents	Dropping of blocks of CO ₂ hydrate and dry ice.
Steinberg & Albanese [28]	SI	NR	60%, 90%	Seawater	Not feasible: more power is required than is generated by power plant.
Steinberg & Albanese [28]	SSCI	500 m for CO_2 gas 2000 m for liquid CO_2	90% 90%	Monoethanolamine	Cost: 86% of total power. Also proposed disposal of solid CO ₂ .
Steinberg & Cheng [35]	SSCI	500 m and 3000 m	90%	Dow FS-1 alkanolamine	Cost: 17% of total power for 500m, 18.2% for 3000 m
Herzog et al [22]	SSCI	> 700 m	80-100%	Amine solutions	Also considered membrane separation, cryogenic fractionation and air separation/ flue gas recycling. Costs: between 25 and 66 % of total power.
Mitsubishi [26]	SSCI	200m- 500m	NR	NR	Mixing of CO ₂ with water in a pressurised pipeline to give CO ₂ hydrate
Mitsubishi [26]	SSCI	>700m & <700m	NR	NR	Injection of compressed CO ₂
Haugan & Drange [27]	SSCI	200-400 m	NR	NR	Direct injection of pure CO ₂ gas

Table 3. Proposed methods of CO_2 disposal in the ocean

^aSSCI= Scrubbing-Separation-Compression-Injection. ^bDIFG= Direct injection of flue gases. ^cSI= Scrubbing-injection. ^dNR= Not reported.

Table 4. Major ions in seawater

lon	Concentration (g kg ⁻¹)
Cl	18.97
SO4 ²⁻	2.65
HCO ₃ ⁻	0.14
Br⁻	0.065
Na⁺	10.47
Mg ²⁺ Ca ²⁺	1.28
Ca ²⁺	0.41
K^{+}	0.38

Table 5. Comparison between wet limestone FGD and seawater FGD (adapted from

Description	Wet limestone FGD	Seawater FGD
SO ₂ removal efficiency	80-95%	90-98%
By-product	Gypsum	None
Required supporting systems	Wet limestone preparation	Aeration
	Oxidation and dewatering	Neutralisation
Capital cost	100%	75-80%
Operating cost	Medium	Low

[37]).

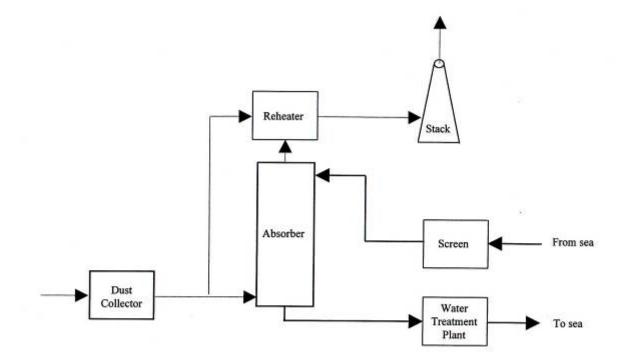


Fig. 1. Flow diagram of a typical seawater based desulphurisation plant.

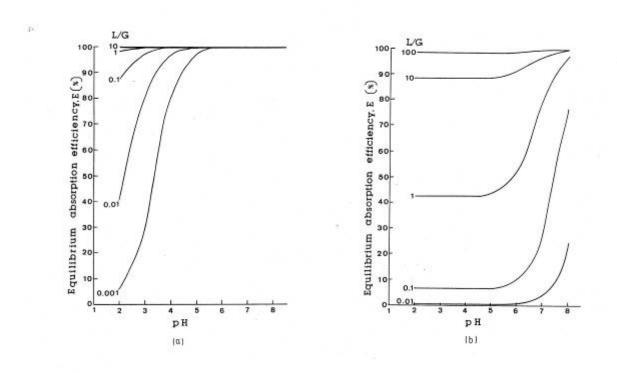


Fig. 2. Equilibrium absorption of (a) SO_2 and (b) CO_2 as a function of pH and volumetric liquid/gas (*L/G*) ratio at 25 ° C.

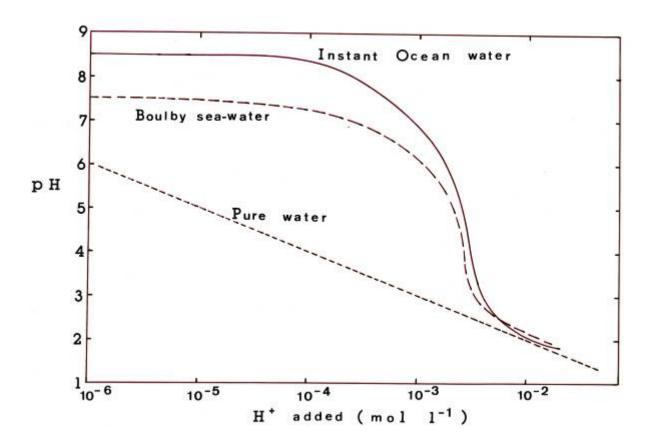


Fig. 3. The buffering capacity of seawater in artificial (Instant Ocean) and natural (Boulby)

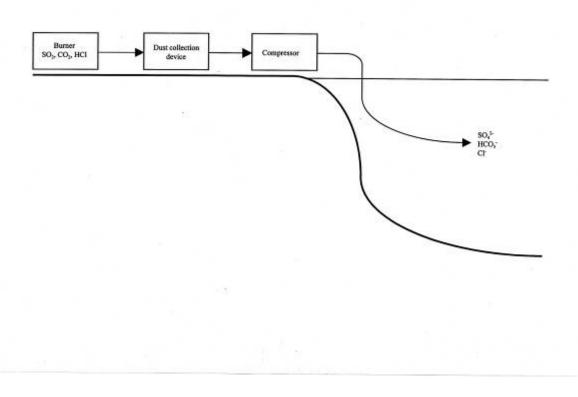


Fig. 4. Direct injection of flue gases into the sea samples