

# Sea Water Scrubbing – Does it Contribute to increased Global CO<sub>2</sub> Emissions

## INTRODUCTION

This document has been prepared by Krystallon in response to articles in the marine press following an article in The Province Newspaper of Vancouver Canada published on October 7th in which it was stated that sea water scrubbing technology contributes to increased global CO<sub>2</sub> emissions. The facts, and measurements from scrubbers in service, indicate that sea water scrubbing of high sulphur fuel oil not only reduces CO<sub>2</sub> emissions but it also contributes to improved air quality by the removal of a very significant portion of exhaust gas particulate matter.

## IVL SUB REPORT

On September 26th 2007 a document entitled “CO<sub>2</sub> - emission and marine sulphur” published by IVL and authored by Erik Fridell was issued by the Swedish Maritime Administration (SMA). The author of the report, Erik Fridell, has advised that the two page document is an extract of a larger yet unpublished report that has been commissioned by the SMA. The SMA has commissioned IVL to undertake research on the impact of sea water scrubbing and according to Erik Fridell the final report will be not be issued until 2008. Apparently the final report will be based upon literature research and contact with sea water scrubber (SWS) manufacturers and will not contain any original research.

It appears that the press has either received briefings or copies of the report and hence the various headlines and articles. A recent presentation by Erik Ranheim to the International Association of Canadian Shipowners (ICAS) in Vancouver, Canada, prompted the sensational headlines “Cruise-ship pollution initiative actually contributes to problem - \$1.5-million pilot 'scrubber' project fatally flawed, meeting told”<sup>1</sup>. Similarly in October 2007 an IPIECA/IFQC CO<sub>2</sub> workshop was advised by Intertanko that a disadvantage of SWS was increased CO<sub>2</sub> emissions, when compared with the use of diesel fuel.

## MARPOL ANNEX VI

In the 1980s the Norwegian and Swedish Maritime Administrations raised issues of acidification in Scandinavia harming forests and fauna. These nations called for regulations to control the emissions to air from shipping. The outcome was the development and completion of Marpol Annex VI in 1997 and the subsequent ratification and entry into force in May 2005. In the 1990s views on the need for a cap on marine fuel sulphur were polarised and the outcome was a very minor reduction from the previous fuel specification limit of 5.0%S to 4.5%S. However the concept of SO<sub>x</sub> Emissions Control Area, (SECA), was agreed as a cap on marine fuel sulphur of 1.5%S in particularly sensitive areas. The Baltic SECA entered into force on May 11, 2006 and the North Sea SECA will enter into force on November 22, 2007. As an alternative to the use of low sulphur fuel Regulation 14 of Marpol Annex VI allows for the use of SWS. In general all IMO regulations allow for equivalency and Regulation 14 is no exception allowing for “any technological method that is verifiable and enforceable to limit SO<sub>x</sub> emissions to a level equivalent to that described in...”

<sup>1</sup> The Province, C. Montgomery, published October 7. 2007  
<http://www.canada.com/theprovince/story.html?id=438279ef-ec5e-42b0-a582-3cce6a54df75&k=39562>,

During the late 1990s Shell undertook two trials of sea water scrubbing installed on board a coastal tanker and also a Norwegian Ferry. The results for the trials demonstrated the effectiveness of SWS at removing SO<sub>2</sub> from exhaust gases and an independent assessment by Marintek a leading Norwegian Maritime Research Centre indicated no significant impact upon the marine environment. The research papers make no mention of the neutralising processes or the evolution of CO<sub>2</sub> during neutralisation. Back in the 1990s climate change was not considered as prominently as it is today so it is not surprising that additional energy consumption or CO<sub>2</sub> evolution were not considered an issue.

### SEA WATER SCRUBBING ENVIRONMENTAL IMPACT ASSESSMENT

Krystallon has undertaken extensive Environmental Impact Assessment (EIA) studies on a sea water scrubber installed on a 1 MW auxiliary engine on the ferry *The Pride of Kent*. These studies have been performed by researchers at the Terramare Institute and Newcastle University lead by Dr Brigitte Behrends. The first two EIA reports are available on the Krystallon web site ([www.krystallon.com](http://www.krystallon.com)). Krystallon is also undertaking further EIA studies on *The Pride of Kent* in support of development of the IMO wash water criteria and is also working in partnership with Holland America Line to study the sea water scrubber on an 8 MW diesel generator on the cruise ship *ms Zaandam*.

The Krystallon sea water scrubber is designed to remove virtually of the entire sulphur dioxide and the vast majority of particulate matter from diesel engine exhausts. No specific measurements have been undertaken but physical and chemical data would suggest that there is no or limited solubility of other gases emitted from diesel engines such as nitrogen oxides, carbon monoxide and carbon dioxide.

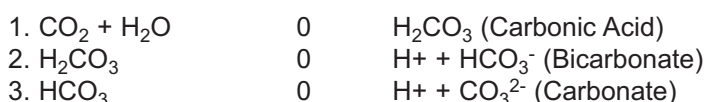
The constituents of the exhaust gases that are scrubbed (removed from the exhaust stream) are either dealt with by processing the scrubbing water (wash water) or by natural reactions in sea and fresh water. Of the latter the principle reaction is the neutralisation of the SO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> by carbonates and other compounds existing in the wash water.

### NEUTRALISATION PROCESS

The majority of neutralisation is provided by carbonates in the seas, oceans, and coastal waters, however about 4.0% of the neutralisation is provided by borates and other ions in low concentrations.

The process of neutralisation follows the following generally accepted paths.

CO<sub>2</sub>, pH and carbonates are all related by the following three equations:



Addition of acids (increasing H<sup>+</sup>) shifts the equations to the left, which at the end leads to a release of 1 molecule CO<sub>2</sub> per proton added.

### CO<sub>2</sub> EVOLUTION FROM THE NEUTRALISATION PROCESS

Considering the reactions above in terms of relative SO<sub>2</sub> evolution based upon 1 tonne of marine heavy fuel oil with a global average 2.7% S content is as follows;

2.7% S = 27 kg sulfur/tonne of fuel

Moles sulphur (32 g/mol) = 843.75 Moles S

1 mole SO<sub>2</sub> results in 1 Mole H<sub>2</sub>O<sub>4</sub> which has 2 protons, therefore creates 2 Moles CO<sub>2</sub> according to the equations above.

The neutralisation of sulphur can produce 1687.5 Moles CO<sub>2</sub> = 74.25 kg CO<sub>2</sub> if the equilibrium would be shifted all the way.

Taking into account that about 4% of neutralisation is undertaken by Borates and other compounds the amount of carbonate alkalinity is thus only 96% of the neutralisation process. Multiplying the CO<sub>2</sub> evolution by this factor of 0.96 from a 100% carbonate process reduces the emission to 71.28 kg CO<sub>2</sub>. Hence 1 tonne of 2.7% S fuel may evolve 71.28 kg of CO<sub>2</sub> through a neutralisation process with bicarbonates. Due to the reduction in bicarbonate, some protons will be consumed through reaction 3, producing more bicarbonate. The equilibrium constants are such that this reaction will only occur to a small extent, but this will nevertheless further reduce the amount of CO<sub>2</sub> that will effectively be released.

### THE ALTERNATIVE TO SCRUBBING SO<sub>2</sub>

The alternative to removing SO<sub>2</sub> from emissions to air is to remove sulphur from the residual fuel oil prior to usage. There are several studies which assess this option. Although it is technically feasible, no large scale residue desulphurisation units exist that produce LS heavy fuel oil for the marine market. But more importantly the studies have concluded that the economics of residue desulphurisation are extremely unattractive. Uncertainty of price and the often negative refinery margin limit are likely to preclude the very significant investments required.

However distillate is an alternative fuel which can be supplied with a low or zero sulphur content. Distillate fuel has a lower density than residual fuel oil and it also has a higher energy content, (HFO circa 40MJ/kg, Diesel Oil circa 42MJ/kg). Whilst HFO is the untreated component of crude oil remaining after vacuum distillation, distillate undergoes several refinery process all of which utilise refinery energy to produce the finished product. Thus it is important to consider both the specific energy of the respective fuels and the energy required to process the products. The preferred method of doing this is to normalise CO<sub>2</sub> emissions for fuels on a per unit of energy basis.

### NORMALISING CO<sub>2</sub> EMISSIONS FOR SPECIFIC ENERGY

The following table is based upon data provided by Concawe. The two fuels are a 3.15%S residual fuel oil and a 0.4%S diesel oil.

Fuel	Combustion CO <sub>2</sub> kg/t	Neutralisation CO <sub>2</sub> kg/t	Total CO <sub>2</sub> kg/t
HFO	3182	83	3265
DO	3174	11	3184

The following table considers the specific CO<sub>2</sub> emission based upon energy. The scrubber energy consumption is assumed to be 2% of fuel consumption.

kgCO <sub>2</sub> /GJ	Neutralisation	Scrubber	Combustion	Refinery <sup>1</sup>	Total
HFO	2.04	1.56	78	0	82
DO	0.24	0	74	10	84

<sup>1</sup> Refinery CO<sub>2</sub> emissions incremental over base case

Although the scrubber incurs CO<sub>2</sub> emissions of 2kg/GJ for neutralisation and 1.6kg/GJ for scrubber additional fuel consumption, this is significantly less than the 10kg/GJ of CO<sub>2</sub> emitted by the additional refinery processing of the distillate.

The reader should consider that carbon content of the fuels, the energy content of the fuels, the most severe CO<sub>2</sub> evolution from neutralisation and a conservative value for scrubber energy consumption are provided in good faith, recognising that any of these values may vary by a few percentages points. The allocation of energy to residual fuel at a refinery is based upon Concawe figures for average emissions and may vary from refinery to refinery.

## OTHER CONSIDERATIONS

- The data used to calculate the evolution of the CO<sub>2</sub> from sea water is likely to be conservative. Test work undertaken by Terramare has indicated that the actual capacity of sea water to accommodate neutralisation is significantly greater than by theoretical analysis.
- No allowance has been given to the absorption of a portion of the CO<sub>2</sub> evolution by the sea water and its ultimate fixing by marine organisms, noting that CO<sub>2</sub> capture by oceans happens at the surface whereas with scrubbing CO<sub>2</sub> is being introduced into the ocean at depths of 3 to 10 metres below the surface.
- The minimum amount of water required by scrubbers is approximately 25t/MW. This volume is fixed by the requirement to cool the exhaust gas. This volume is approximately 1/3 the current volume used in conventional sea water scrubbers. Clearly with further scrubber development reductions in water flow will provide a commensurate reduction in energy required for operation, (perhaps cutting energy requirements by 50% in the future).
- Consideration must also be given to the natural cycle of sulphur compounds. Although it would appear that today sulphur production, (mainly from desulphurisation of natural gas) is beginning to exceed demand, there is nevertheless significant use of sulphur for the production of sulphuric acid, fertilisers and other industrial materials. Inevitably many of these applications of sulphur result in later oxidation and the subsequent neutralisation by natural processes, (eg the use of sulphuric acid to pickle steel results in a process of neutralisation which evolves CO<sub>2</sub>). By removing sulphur from fuels at the refinery does not necessarily guarantee that subsequent processing will not result in the evolution of CO<sub>2</sub> during eventual neutralisation.
- In future scrubbed exhaust gases may replace the provision of Inert gas Plant on tankers, providing a cleaner inert gas suitable for use with clean products and coated tanks as well as for crude oil. This will obviate the need burn diesel fuel to make inert gas and significant CO<sub>2</sub> emissions.

## CONCLUSIONS

It is clear from the careful assessment of the factors involved in sea water scrubbing and the factors involved in the production of diesel oil, that there appears to be a net CO<sub>2</sub> benefit from the use of high sulphur fuel oil and scrubbers.

Ships not fitted with scrubbers and using diesel fuel will release to atmosphere as SO<sub>2</sub> any sulphur contained in the fuel. Ships using high sulphur fuel and fitted with scrubbers will reduce emissions of SO<sub>2</sub> to virtually zero. In addition, particulate emissions are significantly reduced, further contributing to improvements in air quality.

On-going development of scrubbing technology will inevitably lead to lower energy demand and may in the future be capable of scrubbing out other gases such as nitrogen oxides (NO<sub>x</sub>). By the use of scrubbing and other after-treatment technologies, the "zero emissions" ship capable of consuming available fuels is a distinctly feasible long term objective.