COST EFFECTIVE MARINE EXHAUST ABATEMENT FOR NO_X, SO_X AND SOOT

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ABSTRACT

This paper bridges controversy surrounding marine open loop exhaust gas scrubbing restrictions. The solutions offered in this paper apply equally well to both open and closed loop scrubbing methodology. The chlorine dioxide (ClO_2) based gas/mist scrubbing technology presented in this paper works equally well in open and closed loop applications. This ClO_2 based gas/mist phase exhaust scrubbing technology effectively removes more than 99% of SO_X and most of the organic compounds including polycyclic aromatic hydrocarbon compounds (PAH) that create soot in marine exhaust. The very same ClO_2 based gas/mist scrubbing equipment can also be configured to simultaneously treat SO_X and NO_X, plus most of the organic compounds that create soot. Where permitted, the sulfur based salts generated from the ClO_2 based gas/mist SO_X abatement process can be discharged directly into the sea without the typical additional washwater treatment required when SO_X is treated with seawater scrubbers. Alternatively, when closed loop scrubbing is required, this ClO_2 based gas/mist scrubbing process can store the sulfur based SO_X reaction products as a very low volume paste until the ship is in a location that allows paste to be discharged into the sea. The scrubbing device is a simple cylinder that fits into the ship's funnel and a small skid of equipment plus chemical storage that can be configured together or separately in the mechanical area of the ship. Overall, this equipment has a small physical size, high removal efficiency, and low equipment/operating cost. This ClO_2 based gas/mist phase scrubbing technology can be combined with existing abatement equipment or used on its own. The ClO_2 based gas/mist scrubbing technology is in full compliance with IMO regulations for SO_X, NO_X and soot.
Keywords: exhaust, scrubber, open-loop, closed-loop, chlorine dioxide, SO_X, NO_X, soot.

1 INTRODUCTION

The ClO_2 based marine exhaust gas treatment process has 6 distinct features:

- The SO_X scrubbing byproducts from this ClO_2 based gas/mist scrubbing method can be discharged directly into the sea. It does not require the secondary washwater treatment used when SO_X is scrubbed with seawater.
- When a ship is operated in a zone that requires closed loop SO_X scrubbing, the sulfur based salts and treated soot precursors can be temporarily stored as low volume paste until the vessel reaches an area that authorizes discharge of the sulfur based salt paste into the sea.
- Where required, this very same equipment can treat SO_X, and NO_X and some organics that are soot precursors. The change only requires a variation in the ClO_2 dosing rate.
- NO_X scrubbing byproducts are stored as low volume paste that is separate from SO_X scrubbing byproducts with very low cross contamination levels.
- The generation of paste from SO_X or NO_X scrubbing is done with a low energy process that recycles its reactants. The H_2O returns to the scrubber and the salts become paste. The segregation of salts from recirculated scrubbing liquor is so energy efficient that it is done with the differential temperature provided by seawater and engine exhaust. There is also a nominal need for electrical power to operate conventional pumps.

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- The ClO_2 used in the gas/mist phase SO_X or SO_X and NO_X scrubbing processes is the compound that selectively reacts with organic compounds including the polycyclic aromatic hydrocarbons (PAH) [1], [2] which become soot in marine exhaust gas stream. This is explained in greater detail in the body of this paper.

The exceptional SO_X and soot, or SO_X and NO_X and soot removal efficiency of the ClO_2 based gas/mist phase scrubbing technology described herein is possible in large part because the process overcomes the solubility challenges of the target compounds in the exhaust gas. The process utilizes gas phase reactions to treat compounds that have low or no solubility in H_2O, for example nitrogen monoxide (NO) and PAH's. The mist phase of this process reacts with compounds that are soluble in water, for example SO_X and NO_2. The result is greater than >99.8% removal efficiency for SO_X and NO_X [3] and appreciable removal of PAH. The PAH removal efficiency varies with fuel type but is always less than the 50 ug/L IMO requirement for PAH's [4].

The ClO_2 based gas/mist scrubbing technologies ability to capture sulfur or nitrogen salts as separate pastes is another technological breakthrough. The proprietary process includes a closed loop that recycles an intermediary compound that promotes the precipitation of salts from scrubber liquor before they reach conventional saturation. If required, the paste can be dehydrated to granular powder with the addition of a conventional hot air spray dryer or similar technology.

2 CLO_2 BASED GAS/MIST SCRUBBER CHEMISTRY

The same reaction chamber is used to selectively treat SO_X or SO_X and NO_X compounds. Differences in the reaction rates make this selective removal possible. The SO_X reactions can be summarized as described in eqns (1) and (2):

$$5\ SO_2 + 2\ ClO_2 + 6\ H_2O \rightarrow 5\ H_2SO_4 + 2\ HCl, \tag{1}$$

$$SO_2 + 2\ NaOH \rightarrow Na_2SO_3 + H_2O. \tag{2}$$

Chemical cost savings occur by utilizing the NaOH as described in eqn (2) as the first reactant with SO_X and then introducing only as much ClO_2 according to eqn (1) as required to complete the SO_X removal.

The ratio of NaOH to ClO_2 as well as the volume of both is regulated by multi sensor technology and process control logic (PCL) programs that optimizes chemical use. Inlet and exhaust gas SO_X concentrations are compared along with reaction liquor pH and other variables in real time.

The NO_X reactions are summarized in eqns (3)–(5).

$$5\ NO + 2\ ClO_2 + H_2O \rightarrow 5\ NO_2 + 2\ HCl, \tag{3}$$

$$5\ NO_2 + ClO_2 + 3\ H_2O \rightarrow 5\ HNO_3 + HCl. \tag{4}$$

There are differences in the rate of reaction between eqns (3) and (4). Eqn (3) is faster. The difference in reaction rates is adroitly utilized by additional sensor technology and PCL program logic to equalize the NO and NO_2 ratio in preparation for NO_X abatement with the lower cost chemicals as described in proprietary eqn (5).

$$2\ NaOH + NO_2 + NO + (**) \rightarrow 2\ NaNO_2 + H_2O, \tag{5}$$

(**) Options:

- H_2O_2 = 85–90% removal efficiency;
- O_3 = 95% removal efficiency;
- NaOCl = 90–95% removal efficiency;
- $Ca(OCl)_2$ = 90–97% removal efficiency.

$$2\ NO_2 + 2\ NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O. \quad (6)$$

The compounds identified by ** enhance the eqn (5). They are provided to promote the reaction and are supplied in quantities that are a small percent of the NaOH. Eqn (5) includes several options for process promoters. The choices provide alternatives where a client or regulatory agency has an objection or preference.

The reaction with NaOH described in eqn (6) is presented because it occurs but at a much slower rate than eqn (5).

The process control logic allows eqns (5) and (6) to pre-treat the SO_X gas stream because they are less expensive, then ClO_2 is added to the mist to achieve a removal efficiency of >99.8% SO_X that is not possible by eqns (5) and (6).

As noted, the chemical dosing in the ClO_2 based gas/mist scrubbing system is regulated with sophisticated sensor/process control technology. However, the scrubbing technology includes a "polishing module" with chemistry that removes any unused ClO_2. The chemistry of this polishing module eqn (7) also contributes to removal of any stray SO_X or NO_X per eqns (8)–(10)

$$10\ Na_2S_2O_3 + 2\ ClO_2 + 4\ H_2O \rightarrow 2\ NaCl + 5\ Na_2S_4O_6 + 8\ NaOH. \quad (7)$$

The sodium tetrathionate ($Na_2S_4O_6$) formed in eqn (7) is reported on MSDS to not be a carcinogen. There is no reported environmental fate or toxicity.

The acids generated in eqns (1), (3) and (4) are removed according the eqns (8)–(10) shown below. Once again, the sensors and process control monitor the pH of the washwater and gas sensors monitor the target compounds in the gas stream to optimize chemical usage and ensure the exhaust gas and washwater quality are within IMO compliance

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O, \quad (8)$$

$$HCl + NaOH \rightarrow NaCl + H_2O, \quad (9)$$

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O. \quad (10)$$

3 FORMATION OF MARINE SOOT

Literature teaches us that the formation of soot is a progressive process that occurs in the in the engine and exhaust ducting. It begins with smaller organic compounds, for example benzene, toluene, acetylene and 2–3 ring PAH's agglomerating. Large soot particles are formed when these "building blocks" combine to form molecules with mass between 500 and 1000 amu. ClO_2 has the ability to react with many of the organic soot precursor compounds and prevent them from agglomerating. Fig. 1 describes this reaction process between ClO_2 and phenanthrene (3 attached benzene rings) a challenging compound to scrub due to its very low solubility in water (1.6mg/L) and relative inertness in an ocean environment. Fig. 2 described the enhanced reactivity and solubility introduced into the parent phenanthrene by substitutions that result from the reaction with ClO_2.

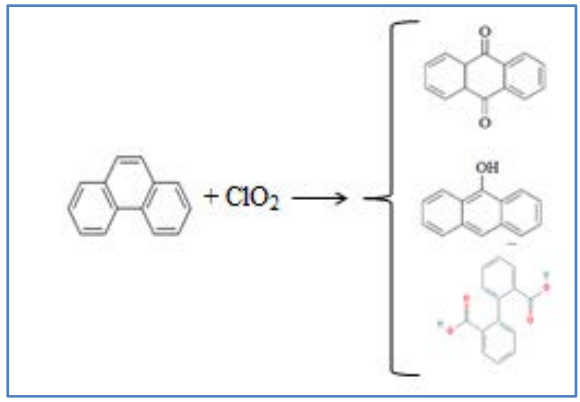

Figure 1: Examples of ClO_2 reactions with phenantherene [2].

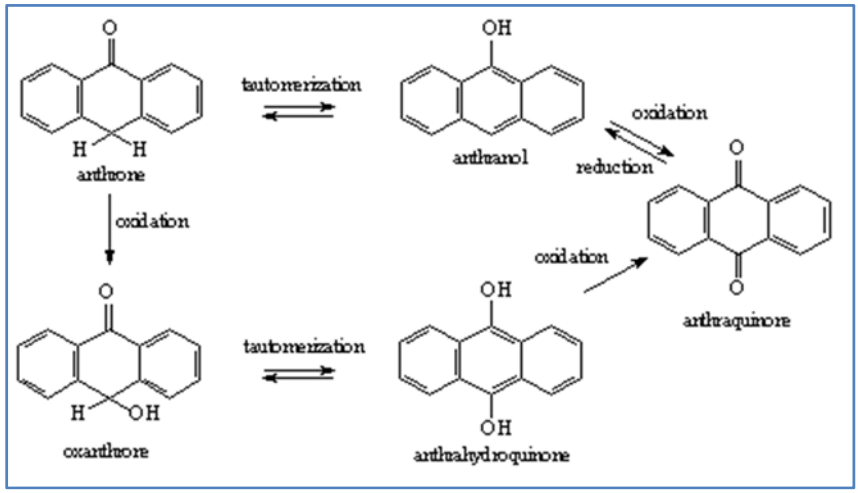

Figure 2: Post ClO_2 reactions with phenantherene [2].

Fig. 3 is an excerpt from an article [5] in which the authors describe the soot formation process in detail. This figure elaborates on the summary provided in the previous paragraph.

> "The molecular precursors of soot particles are thought to be heavy HAHs of molecular weight 500–1000 amu. The growth process from smaller molecules such as benzene to larger and larger PAH appears to involve both the addition of C_2, C_3 or other small units, among which acetylene (C_2H_2) has received much attention, to PAH radicals, and reactions among the growing aromatic species, such as PAH–PAH radical recombination and addition reactions. In experimental studies, PAHs have been found to be the dominating compounds in the sooting zone of premixed flames as well as other combustion environments. The role of ions and fullerenes in soot formation is currently under discussion as well. Comprehensive reviews and literature regarding soot formation are available.

After the early work of Berthelot, who suggested the formation of benzene via direct polymerization of acetylene, and bone and Coward, who hypothesized a potential role for CH_2 and CH fragments, there are several possible reaction pathways leading to the first aromatic ring formation in the gas phase" [5].

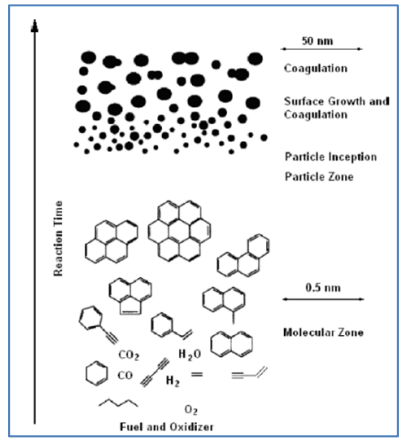

Figure 3: Formation of Molecular Precursors of Soot [5].

Example Reactions with PAH's are shown graphically in Figs 1 and 2. The equations reflect actual reaction products but the diagrams are not balanced.

Once the phenanthrene has reacted with ClO_2 the products with substitutions have enhanced reactivity and solubility. These reaction products undergo further decomposition in an ocean environment. Examples are shown in Fig. 2.

The important point is that this ClO_2 based gas/mist phase scrubbing technology reduces the formation of soot by reacting with a sufficient portion of the organic compounds that are precursors to large soot molecules. The efficiency of the ClO_2 reaction with organics varies with fuel types, but in all samples tested to date, the PAH concentration in washwater was less than half of the IMO's maximum 50ug/L concentration limit.

The ClO_2 based gas/mist scrubbing process removes the soot precursor compounds in the same reaction chamber and at the same time it is reacting with SO_X or SO_X and NO_X. This process is sufficiently effective to allow discharge of the SO_X reaction products to be introduced directly into the sea without further treatment. This process has no need for the post scrubbing treatment of wastewater that is required when seawater is used to scrub SO_X.

As mentioned before, the high removal efficiency success of this ClO_2 based gas/mist scrubbing technology is the result of an effective combination of gas and mist phase reactions. The gas phase has reaction advantages with compounds that are not soluble in water and the mist phase reactions are applicable to water soluble compounds. However, this is just a generality. The success is in the details. The narrative associated eqns (1)–(10) described complexities in mist combinations necessary for this process to achieve its exceptional removal efficiency.

4 CLO_2 BASED GAS/MIST SCRUBBING EQUIPMENT

Fig. 4 describes the general components of this scrubbing process. The graphic depicts the standalone option for this technology. The ClO_2 gas/mist scrubbing process is quite

adaptable, other design configurations are available. Furthermore, the reaction chamber can be oriented in any direction because it does not have a liquid scrubber sump. This ClO_2 based gas/mist scrubbing will not have any operational problems associated with dramatic changes in ship angle during a storm conditions. Such angular deviations would adversely affect a conventional seawater scrubber with liquid sump and packed bed design.

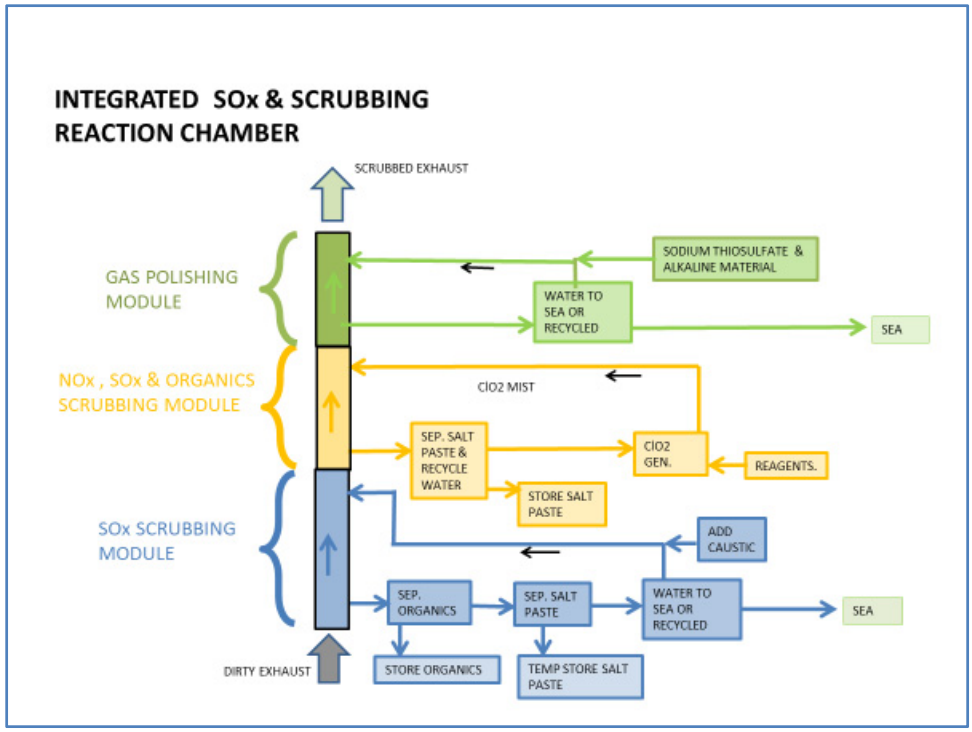

Figure 4: Process flow diagram for the ClO_2 based gas/mist scrubbing system.

5 FIXED AND OPERATIONAL COSTS

The complexity of the equipment supplied by the ClO_2 based gas/mist scrubber is similar to the currently available seawater SO_X scrubber technology. Equipment and installation costs are expected to be similar; however there is another variable that must be considered before an accurate value comparison is made.

None of the seawater based SO_X scrubbers are capable of treating NO_X when required by IMO and national rules. The ClO_2 based gas/mist scrubber can treat both without any upgrades. The ClO_2 based gas/mist scrubber is providing two scrubbers in the space of one and at the cost of one, and also eliminates a second loss of billable sailing time associated with a NO_X scrubber installation in the future.

6 CONCLUSION

When compared to sea water SO_X scrubbing with its inability to effectively treat sludge from organic compounds and limitations associated with closed loop operation, the innovative ClO_2 based gas /mist scrubbing of SO_X, NO_X and organic compounds described in this paper is an intriguing alternative.

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