

## Stack gas scrubbing to meet IMO's 0.5% sulfur bunkering requirement

The International Maritime Organization implemented the IMO 2020 regulations on January 1, 2020. As they pertain to sulfur emissions, the regulations require ships without exhaust gas scrubbers to burn either 0.5-wt%-sulfur fuel (very low sulfur fuel oil, or VLSFO) or 0.1-wt%-sulfur marine gasoil (MGO). Ships outfitted with scrubbers can continue burning 3.5-wt%-sulfur heavy fuel (high-sulfur fuel oil, or HSFO). The economics of installing scrubbers depends very much on the price differential between VLSFO and HSFO.

One analysis<sup>1</sup> reported a \$100/t differential as the tipping point above which installing scrubbers becomes cost-effective, although the figure could be as low as \$75/t. Of course, a decision will depend on the specifics of the ship in question with regard to the ease or difficulty of fitting scrubbers and associated equipment, and therefore the capital cost component. As the demand for VLSFO increases, the price differential is likely to rise over the long term (the effects of COVID-19 notwithstanding), not only from the rising value of VLSFO but also from the falling value of HSFO. This will likely make the scrubber option increasingly attractive.

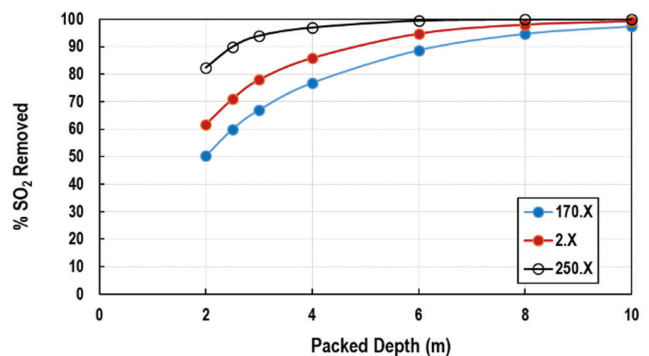
Concern has been expressed by some port authorities about the discharge of sulfur dioxide- ( $\text{SO}_2$ -) laden seawater from open-loop (once-through) systems when ships are close to ports. The alternative is a closed-loop system in which the solvent contains caustic soda or another alkaline medium to absorb and hold the captured  $\text{SO}_2$ . Closed-loop systems are more expensive to operate. However, it is fairly straightforward to switch between closed- and open-loop operation, so there is considerable interest in both systems. In addition to monitoring  $\text{SO}_2$  from the ship's stack, there are compliance requirements for nitrogen oxides ( $\text{NO}_x$ ); this means that monitoring exhaust gas from ships is becoming more akin to monitoring emissions from refineries.

Some interesting learnings can be gained from the simulation of packed absorbers for this service. One is the huge difference between scrubbing with seawater only vs. seawater spiked with caustic soda. Another is the effect of caustic concentration on performance. Yet another is that scrubbing efficiency is mostly a function of the area of the interface between the solvent and the exhaust gas within the scrubber. A fourth is the negative effect of  $\text{CO}_2$  co-absorption, which demands system optimization—maximize the  $\text{SO}_2$  absorption and minimize the

co-absorption of  $\text{CO}_2$ . These aspects of shipboard exhaust gas treating are discussed in a later case study.

**General considerations.** Gas-liquid contacting for the purpose of removing one or more constituents in the gas by absorption into a solvent is usually carried out in a column containing trays or some form of packing (either structured or random). Due to rocking motion (roll, pitch and yaw), treating aboard ships presents special challenges. On land, every effort is made to ensure that columns are closely vertical—a situation that cannot be attained shipboard. Column motion disqualifies trays from serious consideration as contacting devices. Between random and structured packing, structured packing is usually preferred in floating applications (such as FLNG and FPSO) because lateral liquid and gas flows are discouraged by the fact that the structured packing consists of vertically aligned corrugated sheets stacked together. The sheets are an obstacle to the lateral passage of liquid. This helps ensure that gas and liquid flows stay fairly evenly distributed across the column cross-section. In this article, attention is focused on the use of structured packing. However, that is not to say that structured packing is the only contacting device possible. Spray columns are an alternative, but high-performance liquid distributors are still necessary.

A set of spray nozzles uniformly placed over a cross-section near the top of an otherwise empty column can effectively produce a spray of small droplets with large total interfacial surface



**FIG. 1.** Dependence of  $\text{SO}_2$  removal on bed depth and packing size—once-through seawater.

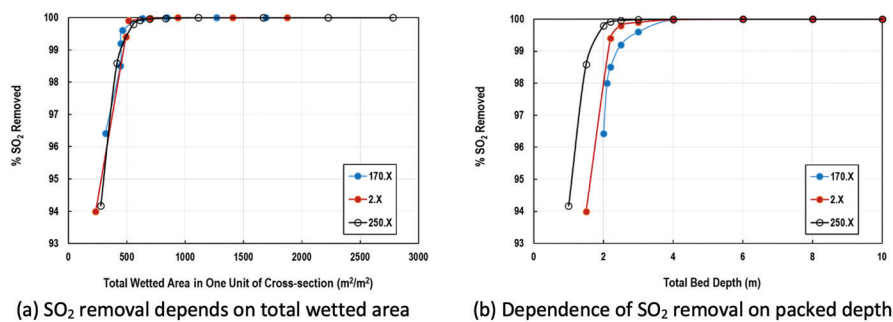


FIG. 2. Dependence of SO<sub>2</sub> removal on bed depth and packing size—1 wt% NaOH.

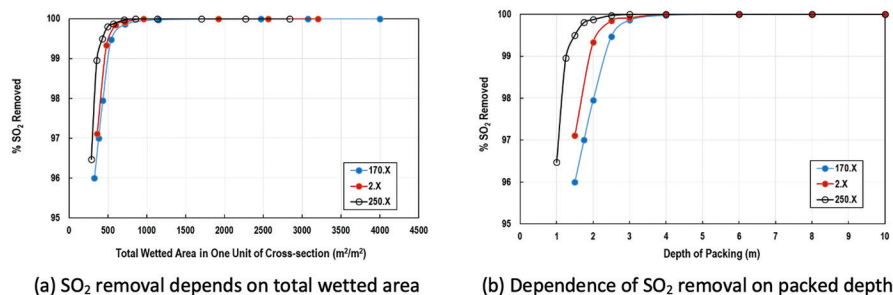


FIG. 3. Dependence of SO<sub>2</sub> removal on bed depth and packing size—15 wt% NaOH.

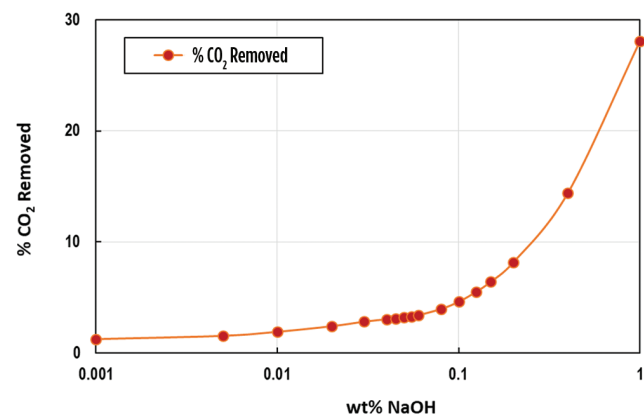


FIG. 4. Using NaOH for SO<sub>2</sub> removal also removes much CO<sub>2</sub>. Calculations are for a 1.5-m deep bed of 2.X packing.

area for contacting the upward-flowing gas. However, droplets tend to coalesce with each other and with the walls of the equipment, so it may be necessary to place spray nozzle batteries at more than one level in the column. The other concern with spray contacting is significant carryover of liquid into the emerging cleaned gas. This may not be a big issue if the solvent is seawater; however, the presence of caustic soda is problematic. Carryover can be controlled with mist pads; these would be mandatory using seawater spiked with caustic. As will become apparent from the case study, only a very short packed bed (or, alternately, a short spray section) is needed when caustic soda is used to enhance SO<sub>2</sub> absorption and the upper part of the column can be used to virtually eliminate mist when treating with seawater.

**Case study.** The specific case is a 76,000-metric-t ship driven by four boiler engines with a combined rating of 67.2 MW

(90,000 hp) running on fuel oil, plus two gas turbines rated at 50 MW total. These data correspond to a Queen Mary-type cruise liner. Only the boiler engines are considered in this example.

Two cases are considered: (1) once-through flow of seawater, and (2) recirculating flow of seawater containing some level of caustic soda. To be specific, the absorber column is assumed to contain one of three sizes of proprietary structured packing<sup>a</sup> (M170.X, M2.X and M250.X). The X-series<sup>a</sup> has lower pressure drop than the Y-series<sup>a</sup> because of its 60° crimp angle, which imposes less engine backpressure. The absorber is sized for 85% of flood, and the packed depth is calculated to achieve the same discharge SO<sub>2</sub> concentration as would be in the stack exhaust if VLSFO (0.5% sulfur) was burned. In other words, about 85% of the SO<sub>2</sub> is to be removed by the scrubbing system when burning HSFO. Note that when using caustic soda, much lower sulfur emissions (> 95% removal) can be easily achieved.

A proprietary simulator<sup>b</sup> contains the components needed to fully describe the composition of seawater. TABLE 1 shows the typical compositions of seawater (100°F) and hot engine exhaust gas (800°F) entering the system. The exhaust gas flowrate was slightly over 42,360 standard cubic feet per minute (SCFM), and the absorber was always sized for 75% of vapor flood. Seawater flow was maintained at 2,000 m<sup>3</sup>/hr, close to the value needed to remove 85% of the SO<sub>2</sub> in a reasonable packing depth with just seawater. NaOH is listed separately in TABLE 1 because it is added to seawater as though it were a molecular entity. Seawater already has an inherent Na<sup>+</sup> concentration tied up with Cl<sup>-</sup> and other ions as part of the charge-neutral ionic soup comprising seawater. Of course, in the mass transfer model, the solvent is treated as an aqueous ionic soup.

**SO<sub>2</sub> removal using once-through seawater.** Simulations were run over the range 2 m–10 m of total packing depth. FIG. 1 shows how the fraction of SO<sub>2</sub> removed depends on both packed bed depth and structured packing size. Note that the packing size designation is roughly the specific surface area<sup>c</sup> of the dry packing in the units m<sup>2</sup>/m<sup>3</sup>, and the designation “X” corresponds to a 60° crimp angle, providing the minimum pressure drop. About 85% of the SO<sub>2</sub> is removed in a 2-m bed of 250.X packing. The M2X size (about 200 m<sup>2</sup>/m<sup>3</sup>) needs a 4-m depth, and 170.X needs between 5 m and 6 m, which means that three times the amount of 170.X packing is needed to achieve the same SO<sub>2</sub> removal as 250.X packing. Column diameter under these conditions is typically 13 ft–15 ft with 170.X, 2.X and 250.X packing, with the finest packing needing the largest diameter.

SO<sub>2</sub> almost always exhibits a very small (usually negligible) equilibrium backpressure, except when the water starts to become nearly SO<sub>2</sub> saturated. Adding caustic soda to seawater not only increases solvent capacity for SO<sub>2</sub>, but it also enhances the absorption rate itself through acceleration by chemical reaction with the high hydroxyl ion concentration of a very alkaline sol-

vent. If the unspent NaOH concentration is high enough, then solvent pH will remain quite high throughout the column. A potential (and as it turns out, quite real) downside is the fact of significant CO<sub>2</sub> co-absorption. In the engine exhaust, CO<sub>2</sub> is present at approximately 65 times the concentration of SO<sub>2</sub>, so despite its lower physical solubility, CO<sub>2</sub> may absorb at a significant rate and parasitically consume a large share of the caustic soda. The higher the caustic concentration, the larger the amount of co-absorbed CO<sub>2</sub> and the larger the fraction of caustic used up by CO<sub>2</sub>. It is, therefore, important to use as low of a caustic concentration as possible.

**SO<sub>2</sub> removal using seawater spiked with NaOH.** Simulations were again run over a range of 1 m–10 m of total packed bed depth using 1 wt% and 15 wt% NaOH in seawater as solvent. FIG. 2 and FIG. 3 show the dependence of SO<sub>2</sub> removal on the depth of three beds of 170.X, 2.X and 250.X packing using 1 wt% and 15 wt% NaOH, respectively. It is apparent that SO<sub>2</sub> removal can be described in terms of total wetted area per unit of tower cross-section, regardless of packing size. It is also apparent that SO<sub>2</sub> removal is, at best, a weak function of packed-bed depth itself. Removing exactly 85% of the SO<sub>2</sub> in the engine exhaust can be a challenge using caustic soda because of the extreme sensitivity of removal to bed depth (and wetted area) when substantially less than complete removal is desired. Exceeding SO<sub>2</sub> removal requirements is, of course, a waste of caustic soda; however, in the interest of meeting the removal goal, a ship's crew inexperienced in operating a small chemical process plant can be assured of compliance by exceeding the *required* removal.

Perhaps the more costly consequence is excessive CO<sub>2</sub> removal when no such removal is required. As FIG. 4 shows, CO<sub>2</sub> removal rises rapidly with the caustic level in the solvent. A 15 wt% NaOH strength will remove nearly 50% of the CO<sub>2</sub> in the stack gas, and even just 1% strength will remove nearly 30% of the CO<sub>2</sub>. Given an exhaust of 14% CO<sub>2</sub> and only 0.216% SO<sub>2</sub>, between 20 and 30 times more NaOH will be used in removing CO<sub>2</sub> than in recovering SO<sub>2</sub>.

**Optimizing the system.** When seawater is used alone as the solvent, determining the flowrate to achieve a given removal of SO<sub>2</sub> is a fairly simple matter using simulation.<sup>b</sup> The key parameter is the total wetted area in the contacting device. A chart such as that shown in FIG. 1 is very easy to generate. Although wetted area is a function of liquid rate, under most commercial conditions wetted area and the physical, or dry, area of the packing are similar enough for practical purposes to allow the dry packing area to be used as a reasonable approximation. A large-size packing is preferred because its lower pressure drop results in the least backpressure on the engine. Once the packing has been selected, the needed bed depth can be readily calculated.

The situation is somewhat complicated when the seawater is spiked with caustic soda. Several factors are at play that make caustic addition attractive, but also more complex:

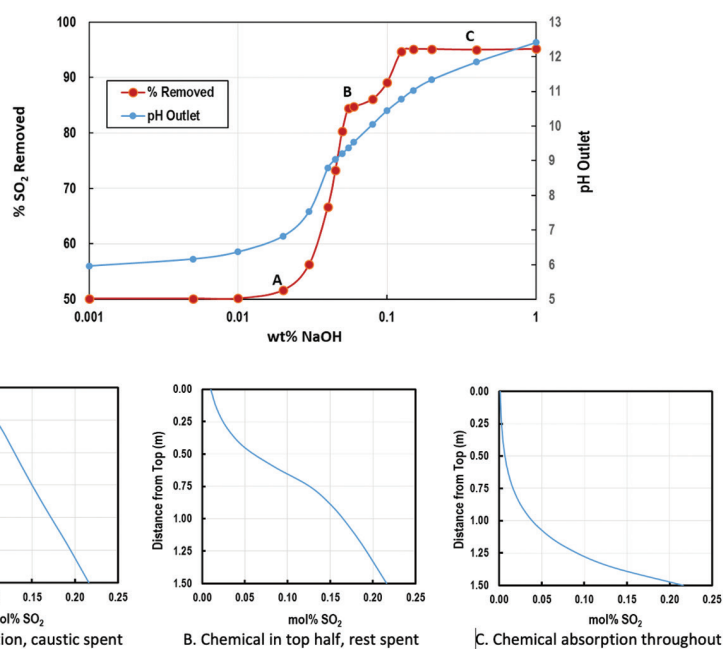


FIG. 5. Types of absorption at various NaOH concentrations. Calculations are for a 1.5-m deep bed of 2.X packing.

TABLE 1. Solvent and gas composition

Seawater, ppmw		Exhaust gas, vol%	
CO <sub>2</sub>	90	H <sub>2</sub> O	11.08
Na <sup>+</sup>	10,800	CO <sub>2</sub>	14.052
SO <sub>4</sub> <sup>=</sup>	2,710	N <sub>2</sub>	74.478
Mg <sup>++</sup>	1,280	O <sub>2</sub>	0.141
Ca <sup>++</sup>	410	SO <sub>2</sub>	0.216
K <sup>+</sup>	399	CH <sub>4</sub>	0.00164
Br <sup>+</sup>	67	CO	0.0046
Sr <sup>++</sup>	80	NO <sub>2</sub>	0.0256
F <sup>-</sup>	1.3		
Cl <sup>-</sup>	19,350		
NaOH	Various		

- NaOH provides high concentrations of hydroxyl ion that react with SO<sub>2</sub> and greatly increase its absorption rate (the pH of seawater is typically 8.1, so the hydroxyl ion concentration is only about 2 ppbw). Therefore, with NaOH, much less packing area (i.e., a much shorter column) is needed to remove most of the SO<sub>2</sub>.
- CO<sub>2</sub> is also absorbed by caustic soda, and since there is roughly 65 times more CO<sub>2</sub> than SO<sub>2</sub>, CO<sub>2</sub> absorption will be a much heavier consumer of caustic unless the packed depth is minimized.
- Keeping the caustic concentration as low as possible will minimize CO<sub>2</sub> co-absorption, but there is a minimum concentration below which the effectiveness of caustic to remove SO<sub>2</sub> falls off rapidly (FIG. 5).
- There is nothing to be gained by having the caustic level any higher than necessary. High NaOH just makes the solution more corrosive, more hazardous to handle, and

more wasteful when the time comes to discharge the solvent overboard after leaving port.

- The best technical approach is to add caustic to the solution gradually, as it is consumed. This means measuring and adjusting the pH. The scrubber system is a small chemical plant that must be operated at sea by operators relatively unfamiliar with process plant operations. Using a chemically reactive solvent certainly does not make the operation any easier to manage.

In the example given here, the SO<sub>2</sub> removal system can be operated satisfactorily with unreacted NaOH concentrations in the column feed above approximately 0.06 wt%, at which concentration only 2%–3% of the CO<sub>2</sub> is co-absorbed. However, the bed depth is only 1.5 m, whereas the depth needed when using seawater alone is 6 m–8 m for around 90% SO<sub>2</sub> removal. Rather than two columns in parallel, it would make greater economic and physical sense to have a single bed with two feed points, one at the top for seawater only and one at the 1.5-m level (in this case) when using caustic soda. The short bed would be on the bottom for use with caustic, and a deeper bed would be on top, with both beds being operated together when using seawater. Liquid distribution should be via spray nozzles, rather than troughs, to alleviate the effect of sloshing from vessel pitch and yaw. Such a system is not difficult to fully automate with push-button switching from seawater to caustic and with caustic addition under pH control to maintain the effluent solvent above a pH of around 6.0.

The simulator<sup>b</sup> is strictly mass transfer-rate based, and is therefore capable of accurately assessing the effect of the particular packing type, its size and material, and even the brand. The results produced are quantitatively accurate, and the effects of changing parameters on performance can be relied upon. The mass transfer rate-based simulation helps optimize SO<sub>2</sub> seawater scrubber design for sound, environmentally responsible operation. **HP**

#### LITERATURE CITED

- <sup>1</sup> Miller, G., "Coronavirus is decimating IMO 2020 ship-scrubber savings," *American Shipper*, March 10, 2020, online: <https://www.freightwaves.com/news/coronavirus-is-decimating-imo-2020-ship-scrubber-savings>

#### NOTES

<sup>a</sup> Mellapak

<sup>b</sup> ProTreat

<sup>c</sup> Specific area is the surface area per unit volume of packing (area/volume)

**PEDRO OTT** joined Optimized Gas Treating Inc. in 2018 as a Senior Applications Engineer in Business Development, providing marketing, licensing and technical support to ProTreat and SulphurPro customers. With over 25 yr of experience, he is an expert in acid gas treating, sulfur recovery, gasoline and distillates hydroprocessing, sour water stripping and LNG. He holds a BS degree in chemical engineering from Simón Bolívar University in Venezuela and a specialization in petroleum refining and gas from IFP School in France. In addition to English, he is fluent in Spanish and French.

**RALPH WEILAND** is Chairman of Optimized Gas Treating. He formed Optimized Gas Treating more than 25 yr ago, and with Australian colleagues developed the ProTreat mass transfer rate-based gas treating simulator, and later the sulfur plant simulator SulphurPro. He holds BSc and MSc degrees, as well as a PhD, in chemical engineering from the University of Toronto.