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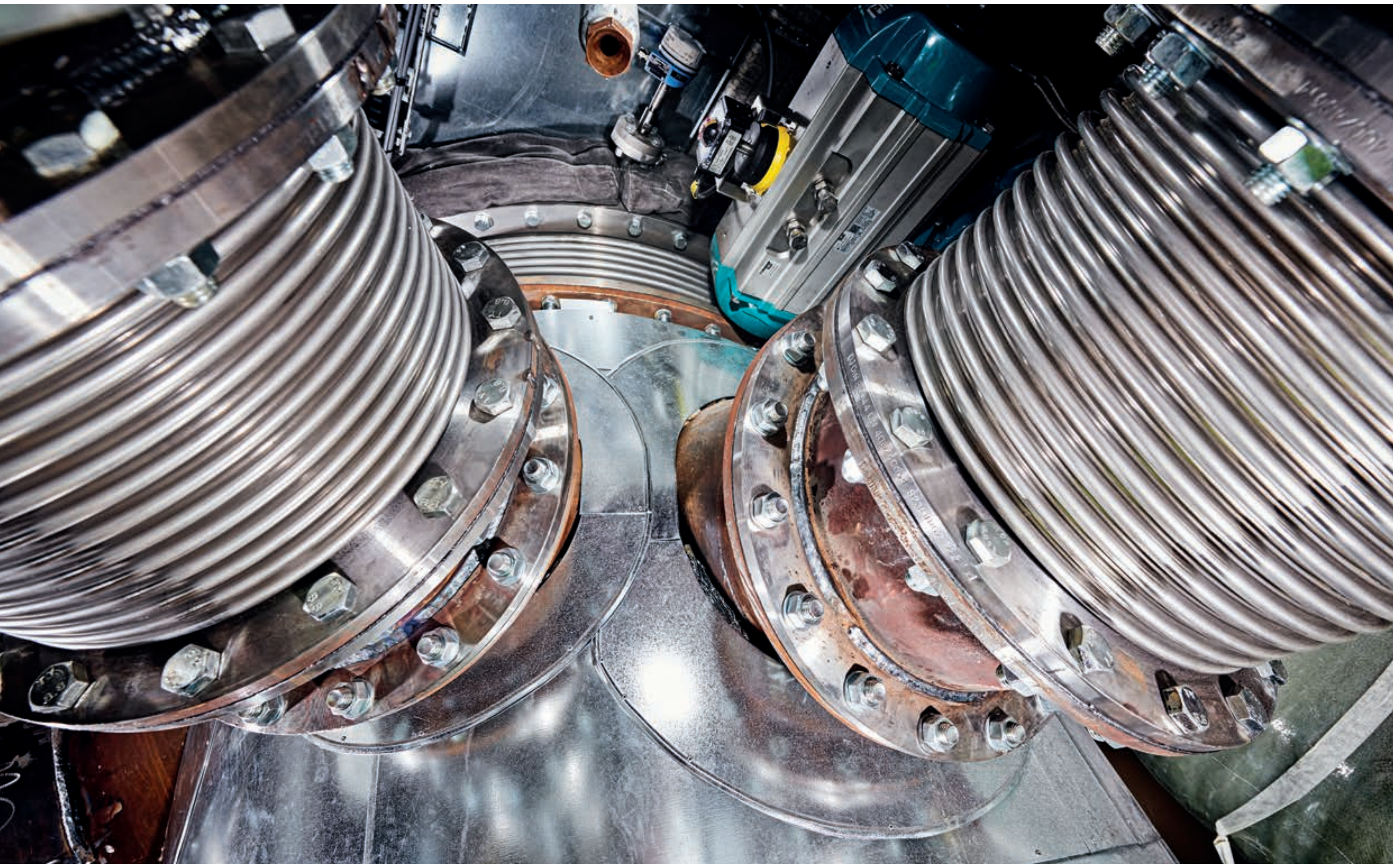

CASE STUDY

MARITIME FLUE GAS DESULPHURIZATION SCRUBBER SYSTEMS **MATERIAL SELECTION**

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LEAKING BELLOWS

THE CONSEQUENCE OF
SELECTING THE WRONG MATERIAL

ABSTRACT

Environmental protection is our common goal and one of these improvements is a new law implemented by INTERNATIONAL MARTIME ORGANIZATION (MARPOL) adjusting Emission Control Areas (ECAs) with current and upcoming Sulphur limits. Sulphur oxides are formed in the combustion process of traditional fuels. As a consequence of this chemical process, we have acid rain which is very harmful to people, environment and infrastructure. Therefore, proper regulation was needed and implemented. To achieve new law requirements, ship owners have to switch to costly low Sulphur fuel, or choose modern technology to clean exhaust gases from Sulphur. This has influence on new ship designs and refurbishment of already existing ships.

Due to the fact that sulphuric oxides dissolve in water, a scrubber system is a good and practical solution. The main point in Flue Gas Desulphurization system based on scrubber, is the selection of right materials for each part, considering that no two ships are the same and are floating on different seas.

The purpose of this document is to present the most common materials used for scrubber systems which are high alloy stainless steels. Based on technical properties and chemical resistance of presented materials the best solution can be featured.

NEED ANY HELP?

If you would like to discuss this topic even further, discuss the issues in your scrubber system or anything else, please feel free to contact our experts on this area:

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INTRODUCTION

Corrosion is a natural process based on gradual degradation of a metal into a more chemically-stable form like oxide, hydroxide or sulfide. This gradual destruction occur by chemical and/or electrochemical reaction with the surrounding environment. When the environment and/or the medium is highly corrosive, carbon steels are not sufficient and stainless steels are often chosen. Although in some conditions they are not immune to it. Whether a stainless steel is corrosion resistant depends on a combination of its chemical composition and the aggressiveness of the environment. [1]

There are two types of corrosion with following details:

TWO TYPES OF **CORROSION**

1. Dry high temperature corrosion

- Oxidation
- Sulfidation
- Carburization and nitridation

2. Wet corrosion

- Atmospheric corrosion
- Galvanic corrosion
- Intergranular corrosion
- Environmentally assisted cracking
- Hydrogen induced stress cracking
- Pitting corrosion
- Crevice corrosion
- Uniform corrosion
- Stress corrosion cracking
- Corrosion fatigue
- Sulphide stress cracking

MATERIALS

Stainless steels for FGD scrubber service are selected on basis of corrosive media, operating conditions, system design and a total economic aspects. Some candidates such as Duplex and alloys stainless steels are listed in Table 1. As we can see in Table 1 all materials, presented, have different chemical compositions and this is a „key point" of material corrosion resistance.

Table 1: Nominal compositions of FGD scrubber alloys

Alloy	EN	UNS Number	Ni*	Cr*	Mo*	Cu*	N*	Fe*	Mn*	Co*	Other*
317LMN	1.4439	S31726	17.5	20	5	-	0.2	Bal.	2	-	0.825
904L	1.4539	N08904	25	20	4.8	1.5	-	47	-	-	-
254 SMO	1.4547	S31254	18.5	20.5	6.5	1	0.22	Bal.	1	-	0.84
2205	1.4462	S32205	6.5	23	3.5	-	0.2	-	2	-	1.05
625LCF	2.4856	N06626	63	23	10	-	0.02	5	0.5	1	5.16
31	1.4562	N08031	32	28	7	1.4	0.25	Bal.	2	-	1.745
59	2.4605	N06059	59	24	16.5	0.5	-	1.5	0.5	0.3	0.535
C-276	2.4819	N10276	63	16.5	17	-	-	7	1	2.5	4.92

* all parameters were presented in max. concentration

Sea water environment, fuel combustion products and chemical additives all those factors that have influence on material corrosion. According to Dittmar's principle: "Chemical composition of sea water and ratio of each elements to another is the same in all seas. Only concentration is different". [2] Based on this rule we can assume the following sea water composition:

- Cl^- (chloride ions) = ca. 19.34 ppt
- Na^+ (sodium ions) = ca. 10,75 ppt
- SO_4^{2-} (sulfuric ions) = ca. 2,7 ppt
- Mg^{2+} (magnesium ions) = ca. 1,29 ppt
- Ca^{2+} (calcium ions) = ca. 0.42 ppt
- K^+ (Potassium ions) = ca. 0,39 ppt
- Other = ca. 0,25 ppt

* ppt – part per thousand

CHEMICAL REACTION

Scrubber systems for Flue Gas Desulphurization are based on sea water which components react with sulphur oxides. Generally chemical reaction is presented in the below equations:

Sulphur oxides reaction with sea water,

(1) $SO_2 + H_2O <> H_2SO_3 <> H^+ + HSO_3^-$

(2) $HSO_3^- <> H^+ + SO_3^{2-}$

(3) $2\ SO_3^{2-} + O_2 <> 2\ SO_4^{2-}$

(4) $2\ SO_4^{2-} + 2\ H_2O <> H_2SO_4 + O_2$

Nitric oxides reaction with sea water,

(5) $2\ NO + O_2 <> 2\ NO_2$

(6) $2\ NO_2 + H_2O <> HNO_2 + HNO_3$

(7) $3\ HNO_2 <> HNO_3 + 2\ NO + H_2O$

On closer observation, when fresh sea water is limited process of receiving sulfur oxides from exhaust gases is amplified with chemical additives,

(8) $2\ Na^+ + 2\ OH^- + SO_2 > Na_2SO_3$

(9) $4\ Na^+ + 4\ OH^- + 2\ SO2 + O_2 > 2\ Na_2SO_4 + 2\ H_2O$

(10) $Na^+ + OH^- > NaHSO_3$

(11) $SO_3 + H_2O > H_2SO_4$

(12) $2\ NaOH + H_2SO_4 > Na_2SO_4 + 2\ H_2O$

Due to above mentioned equations a combination of all those chemical compounds presented in table 2 will be considered as possible to be present during the process.

Table 2: Basic production in scrubber FGD installation using sea water as one of compounds

Name	Chemical formula	CAS	pH	Influence on solution pH	Density [g/cm³]
Sulphuric acid	H_2SO_4,	7664-93-9	0.3	acidified	1.84
Nitric acid	HNO_3,	7697-37-2	<1	acidified	1.4
Sodium sulfate	Na_2SO_4,	7757-82-6	5÷8	neutralize	-
Hydrochloric acid	HCl,	7647-01-0	<1	acidified	1.19
Sulphur dioxide	SO_2,	7446-09-5	-	acidified	-
Sulphur trioxide	SO_3,	7446-11-9	-	acidified	-
Sodium hydroxide	NaOH,	1310-73-2	13.7	alkalized	1.045
Other	-	-	-	-	-

There is no single material appropriate to all scrubber components and all scrubber designs. The corrosion of gas distribution system and their components by corrosive process gases has been problematic in the industry for many years. Pitting and crevice corrosion are the mainly observed types of corrosion in desulphurization environment. Stress corrosion cracking and galvanic interactions are of secondary importance. [3]

Additions like chromium, molybdenum and nitrogen are improving resistance of stainless steel against pitting and crevice corrosion. Additionally, nitrogen increases the mechanical strength without reducing the ductility properties. Table 3 is presenting mechanical properties of considered in this case materials.

MATERIAL PROPERTIES

Table 3: Mechanical properties of FGD scrubber alloys

Alloy	EN	UNS Number	Yield Strength Rp0,2 [MPa]	Tensile Strength Rm [MPa]	Elongation [%]
317LMN	1.4439	S31726	≥ 240	≥ 550	≥ 40
904L	1.4539	N08904	≥ 220	≥ 490	≥ 35
254 SMO	1.4547	S31254	≥ 310	≥ 655	≥ 35
2205	1.4462	S32205	≥ 450	≥ 620	≥ 25
625LCF	2.4856	N06626	≥ 275	≥ 690	≥ 30
31	1.4562	N08031	≥ 280	≥ 650	≥ 40
59	2.4605	N06059	≥ 340	≥ 690	≥ 40
C-276	2.4819	N10276	≥ 310	≥ 730	≥ 30

* mechanical properties at room temperature

A common laboratory method of comparing corrosion resistant stainless steel and alloys is the determination of the critical temperature above which pitting occurs (CPT), or the crevice corrosion occurs (CCT). Table 4 is indicating results of pitting and crevice critical temperature and pitting resistance equivalent for chosen alloys. However different products and different surface finish may show values that differ from the values given in this table. A rough estimate of the relative influence of these alloy additives on the corrosion resistance can be achieved by calculating the Pitting Resistance Equivalent (PRE). There are different formulas to calculate the PRE number, the most common have either a factor 16 for nitrogen and are used in this case. [3]

(13) $$PRE = \% Cr + 3.3 \cdot \% Mo + 16 \cdot \% N$$

Table 4 Pitting Resistance Equivalent (PRE), pitting (CPT) and crevice (CCT) critical corrosion temperature

Alloy	EN	UNS Number	PRE	CPT*	CCT*
317LMN	1.4439	S31726	39.7	50	5
904L	1.4539	N08904	35.84	40	10
254 SMO	1.4547	S31254	45.47	65	35
2205	1.4462	S32205	37.75	30	20
625LCF	2.4856	N06626	56.32	90	40
31	1.4562	N08031	55.1	85	65
59	2.4605	N06059	78.45	>bp**	50
C-276	2.4819	N10276	72.6	>95	70

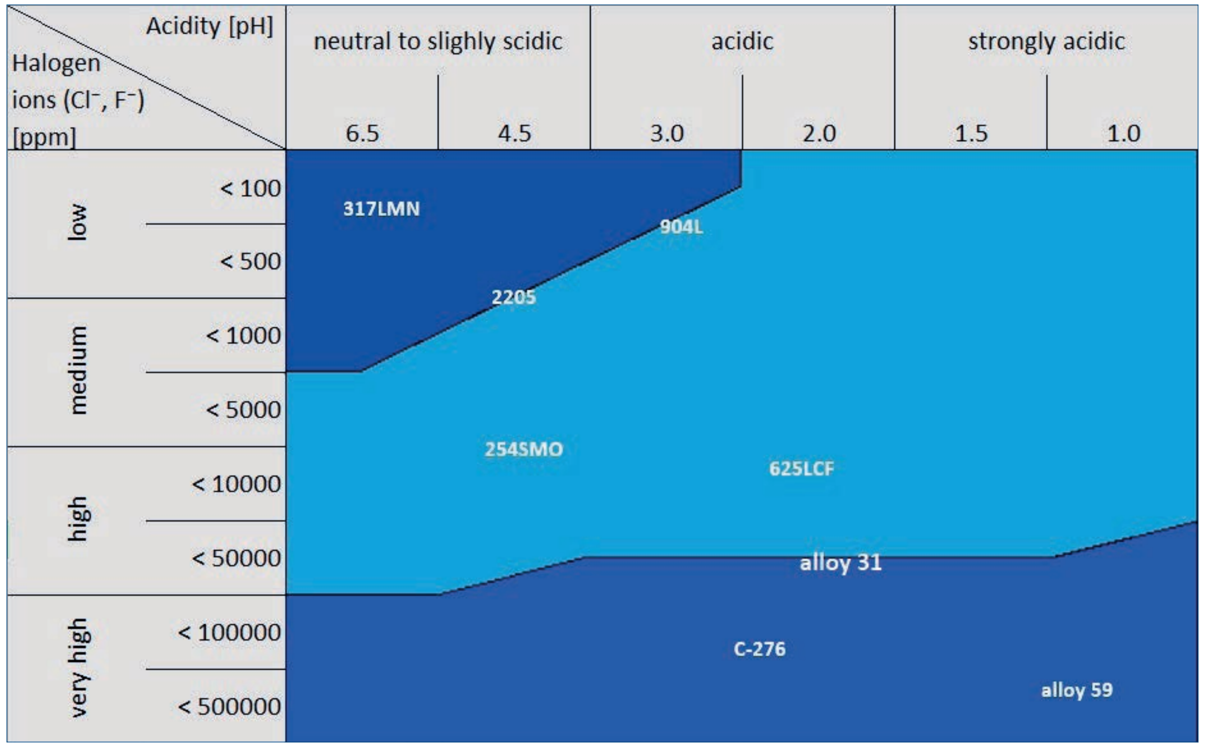
* CPT/CCT values are typical values

** acid boiling point

MATERIAL SELECTION

Corrosion resistance of aforementioned materials is presented on figure 1. Different colors are representing different operating conditions in terms of acidity and chloride and fluoride ions concentration in the temperature range that FGD is normally operating (50-70°C).

Figure 1: Guideline for material selection in Flue Gas Desulphurization



To define most suitable material for flue gas desulphurization system, a few major things should be considered:

- Component location in the FGD system,
- Medium (chemical composition, pH, elements concentration, etc.)
- Temperature,
- Lifecycles,
- Cost price,
- Others.

The most popular material for scrubber system is SMO 254. It could be used in many places in the system, however considering increased temperature or acidity it may have its limitations. Moreover, for high resistance chemical corrosion, influence of chloride ions should be considered as well. Taking into account very high acidity, materials Alloy 59 and C-276 (from Hastelloy group) seem to be the most suitable. Those materials have a high PRE score and very good mechanical properties. For intermediate conditions Alloy 31 and Inconel 625 LCF can be recommend material to be used as well.

SUMMARY

The biggest challenge for the Maritime Industry is to comply with the IMO requirements regarding sulphur oxides up to 2020. Systems existing on the market are utilizing sea water and scrubber system for flue gas desulphurization.

This process is relatively efficient but most of the elements and chemical reaction products are highly corrosive. Difficulty with proper definition of the medium composition with pH and elements concentration incorporates additional corrosion problems. Additional negative factor regarding corrosion issues can be intermittent use of the scrubber system and/or cleaning process maintained under different temperature conditions.

None of the presented materials is completely resistant for acid environment. Selection of suitable material should be based on many aspects like for example:

- Corrosion resistance,
- Welding and forming capabilities,
- Cost,
- Material availability,
- etc.

SMO254 is a relatively good solution for many parts of the scrubber system but should not be recommended when medium temperature is above 65°C with low pH environment.

The best chemical resistance presents Alloy 59 and Hastelloy C-276. Also Alloy 625LCF and Alloy 31 have good chemical resistance and could be considered as optional materials for specific parts of system.

REFERENCES & DISCLAIMER

[1] "Methods of Protecting Against Corrosion" Piping Technology & Products, (retrieved January 2012)
[2] Polish Academy of Sciences, Institute of Oceanology
[3] "Corrosion Handbook", Outokumpu Stainless Steel Oy

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