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Abstract
Production facilities, including platforms or FPSO, are becoming more and more complex structures. Reducing the weight of the process units is an important challenge, and represents a huge source of costs savings.
IFPEN, PROSERNAT and INDUSTEEL have evaluated two alternative metallurgies with high mechanical properties to reduce the weight of equipment of amine gas treating units (AGRU). Duplex stainless steels are considered as an alternative to more conventional austenitic stainless steel grades. High strength alloy steel ASME SA-533 type E class 2, having an UTS above 90 ksi, can be an alternate to carbon steel ASME SA-516 Gr65 type (UTS 65 ksi).
The compatibility of these steel grades with amine service was checked through autoclave corrosion tests in amine solutions. Various experiments were performed in conditions representative of the bottom part of absorber and of upper section of regenerator of AGRU, with variable loadings of CO_2 and H_2S. Study used different specimens: weight-loss coupons, four-point-bend assemblies, and U-bends. For all these tests, alternative metallurgies proved to behave at least as well as the reference ones generally considered in amine plants with no significant corrosion nor cracking.
In addition to experimental tests and presentation of steel properties, the paper describes a case study of AGRU where the mass gain and CAPEX benefits are elaborated for a 75 bar, 4.5 meters diameter absorber, and for a 4.8 meters diameter, low pressure, stripper.

Keywords Alkanolamines; gas sweetening; SA-533 type E; duplex stainless steels

Introduction

The Advamine™ technologies have been developed over 5 decades to propose amine based processes for all types of natural gas sweetening applications. These processes are being licensed through PROSERNAT, Axens Group Company.

These processes are based on widely available open market chemicals and have benefited from oil & gas producer Total a considerable operating experience. This experience, with more than 150 industrial units built represents a large operating feed-back and is based on a large number of shapes of acid gas removal units. It also includes an extensive know-how on performance, solvent likehood and protection against corrosion. Furthermore, Total has had many years of continuous experience of design and operation of AGRU with high acid gas loadings (0.85 – 0.9 mol/mol) thanks to the adjusted selection of materials and the reliable management of corrosiveness of the solution [1-6]. This experience has opened the door to reduced solvent circulation, minimized heat requirements and controlled investment costs of amine technologies marketed under Advamine™ trademark by PROSERNAT.

Generally R&D's activities on amine technologies seek to understand the functioning of the units, including aspects of understanding corrosion and degradation phenomena relative to solvents. Technology providers are innovating on solvent formulation to upgrade the performance of AGRU, which can limit their costs, or open the gate to deeper purification of the treated gas. Numerous researches are also carried out to precise the accuracy of the simulators of amine units, so that users can optimize their design or better understand their daily life.

However, the continued developments in solvent gas scrubbing technologies are not just the matter of solvent performance and simulation tools to ensure the most advanced performance and the most compact designs. Materials and especially steels have made considerable progress in a path to increase the mechanical strength, reducing thicknesses and minimizing weight constraints. Beyond the gains in process design, it is also possible to consider building a given size of equipment of AGRU with stronger materials, requiring smaller thicknesses and dieting their weight.

Recently the PROSERNAT and IFPEN teams have conducted a project with INDUSTEEL ARCELORMITTAL to study materials which reduce the thickness of steel plates and propose gains in the design of acid gas removal units operated with Advamine™ solvents.

Two materials are considered for two separate applications:

- Replace carbon steel (e.g. SA-516 Gr65) on high-pressure equipment with a high thickness, such as the absorber and the drums of the gas section.
- Replace the stainless steels (especially SS316L) on the Regeneration section, composed of low pressure equipment but operating at high temperature (120 – 135 °C) so that the rich solvent is regenerated.

In the first case, it is proposed to use a high strength alloy steel ASME SA-533 Type E Class 2. In the second case, a 2205 Duplex material is proposed.

Within this paper, reference shall regularly be made to process components of an acid gas removal unit (AGRU). As a basic case, which is illustrative for objectives of development and selection of alternatives materials, the schematic Process Flow Diagram (PFD) given in Figure 1 shall be use. The facilities shall always be identified according to this diagram. It is only aimed at being indicative of the major functionalities of an amine unit. It does not include some specific process equipment which may be added to cover the wide variety of gases, process specifications and operating conditions.

The raw gas, containing either CO_2 or H_2S or both acid gases is first treated through a scrubber and/or a filter-coalescer, in order to remove production water and hydrocarbons from the feed gas. It then enters the absorber column, where it circulates in the packed or trayed column, counter-current to an alkanolamine solution. Acid gases components are removed from the raw gas by chemical reaction with the amine. The purified gas is collected overhead the absorber column. From the bottom of the absorber, the rich amine solution flows to the flash drum, where it is flashed to a lower pressure to remove dissolved hydrocarbons and a small portion of the acid gas. The rich amine then circulates through the rich – lean heat exchanger, where it is heated before entering on top of the regenerator column. In the regenerator, acid gases are stripped from the solvent using heat supplied by the reboiler. Acid gases are collected overhead the regenerator. From the bottom of the regenerator, the hot lean amine passes through the rich – lean exchanger, where it is used to heat the rich solution. It is then buffered in the amine tank, where it is pumped back to the absorber for a new cycle.

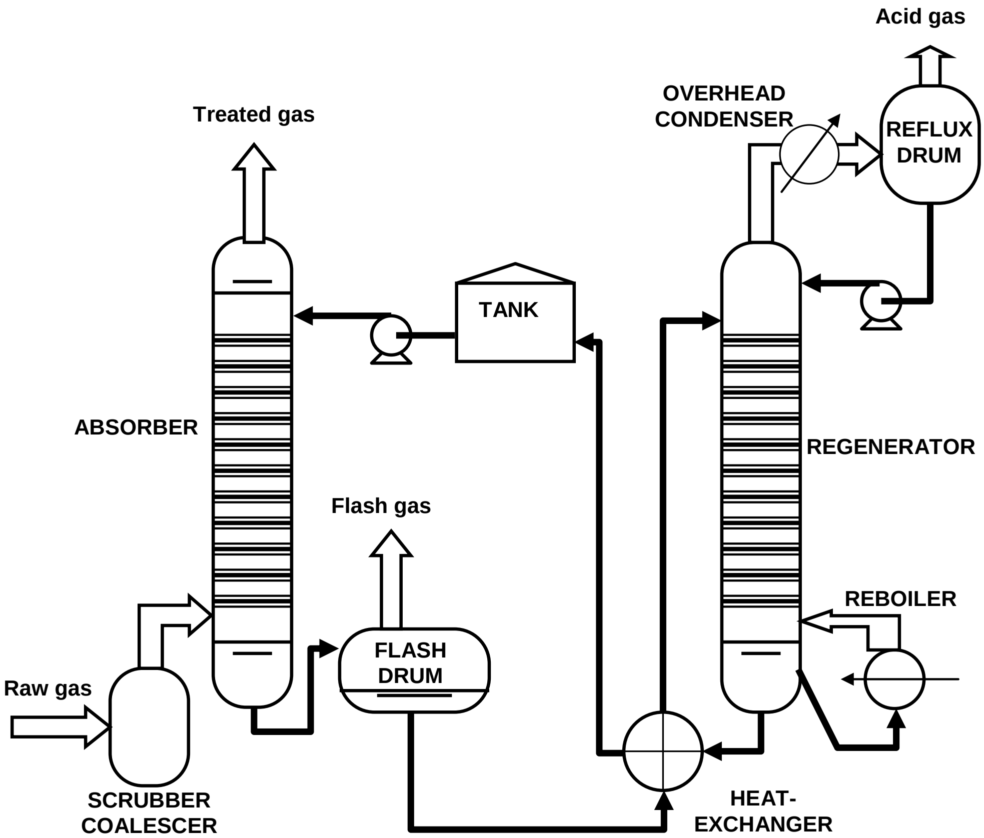


Figure 1 A schematic amine process flow diagram

Industrial objective

The conventional materials of construction of an amine unit are given in the table 1 for the main equipment and lines. The table 1 also indicates the main principles attached to the selection of those steels. This is not a general statement since other criteria may be applied for the selection, like the presence of high content of chlorides (> 500 ppmwt) or a solvent more prone to degradation which generates high content of corrosive Heat Stable Salts (HSS), which can justify the choice of more resistant alloys. The current list corresponds to a "standard" amine unit operating in the field of natural gas treatment with a good protection against degradation (no oxygen ingress, no contamination of the feed gas, moderate temperature). As such, the acid gas loading of the rich solvent stays moderate; the gas has H_2S and CO_2 contents which bring a good protectiveness by resilient layers of iron sulfide deposed on equipment made of carbon steel (CS). The selection of alternate materials discussed in this paper would come as an option to the basic choices of table 1.

Equipment	Material	Selection criteria	Additional process design contraint
HP Absorber Shell Trays	 CS SA-516 Gr65 CS SA-516 Gr65 + SS 316L clad SS 316L	 Low solvent loading High solvent loading > 0.8 mol / mol Avoid erosion/corrosion including CO2 service.	 NACE(HIC) requirement for H_2S service [1], high thickness due to high pressure.
Rich amine lines	SS316L	Avoid Erosion – corrosion due to high velocity / degassing	Offshore application requires alternate to SS316L due to marine environment
Rich – lean heat exchanger	SS316L for plates CS + SS316L clad for panels.	Avoid Erosion – corrosion due to high velocity / degassing	Offshore and marine application requires alternate to SS316L due to marine environment
Regenerator Acid gas overhead + gas cooler Shell Top Bottom shell Internals	 SS 316L CS + SS316L clad or plain SS 316L CS or CS + SS316L or SS316L CS SS 316L	 Wet CO2 service, condensation of water + low H2S, erosion corrosion Jetting of hot rich amine, erosion / corrosion Erosion / corrosion / Acidic corrosion in presence of HSAS. high T° and loading in sweet units	 NACE(HIC) requirement for H_2S service. Offshore and marine application requires alternate to SS316L due to marine environment
Reboiler Shell Heating tubes / tubesheet	 CS or SS316L SS316L / SS316L + CS	 Erosion / corrosion / Acidic corrosion in presence of heat stable salt and amine degradation products.	 Offshore and marine application requires alternate to SS316L due to marine environment

Table 1: material selection of main equipment –amine unit

Any selection of alternative materials shall meet first, and both selection criteria imposed by the process parameters. As such they shall resist to the main and secondary conditions of table 1. The material must of course comply with the codes of construction, inspection and certifications, potentially the codes of repair, imposed by the standards of the project, first of all the ASME Boiler and Pressure Vessel Code (BPVC). The material has to finally and above all withstand the long-term operation with an amine solvent and gases present in the capacities, whether it is a fresh solvent or a degraded which has withstood years of operation.

The validation of alternative materials has therefore proceeded in three steps:

- Proposal of alternate materials by INDUSTEEL. They can reduce the weight of the equipment and comply with all the standards and criteria for the selection of materials in an amine unit, as well as the constraints relative to stamping and certification.
- With the support of INDUSTEEL, the completion of a study of the proposed materials taking into account the existing references, the fabrication, welding and approval procedures, and the feedback of fabrication manufacturers using these materials.
- Test of corrosion resistance carried-out by IFPEN; Those have been made by long exposure to amine solutions representative of the operating conditions in the high pressure absorber (H2S + CO2 loaded amine, temperature 60-90°C) and regeneration (low pressure temperature 120-140°C). Solvents can be loaded in H2S and CO2 and be previously degraded by contact to oxidant. On this subject, the study has followed a protocol identical to the one which studied the corrosiveness of various solutions of amine solvents and the comparison of a solvent artificially degraded by the effects of temperature, high loads of CO2, H2S, oxygen to a solvent directly sampled on unit in operation [2].

The study has finally evaluated the economic interest in using these alternative materials in acid gas removal units, instead of SA-516 Gr65 and SS316L.

SuperElso®

SuperElso® concept was developed 20 years ago, aiming at providing end users with high strength steel with excellent weldability in order to reduce the weight of vessels. Many vessels were fabricated using SuperElso® 500 material in North Sea or West Africa offshore projects, for which weight reduction was of paramount importance.
Further improvement of SuperElso® 500 was done in the 2000's to get a material with improved low temperature CVN impact toughness and suitable for use in wet-H_2S containing environment ("sour service"). This material branded as SuperElso® 500HIC was used to fabricate high pressure separators and adsorbent vessels for FLNG projects. Since 2013 SuperElso® 500HIC material has been available in ASME BPVC as SA-533 type E material, and Industeel produces this material under the name SuperElso® 533E [3].

Characteristics of the steel

SuperElso® 533E corresponds to ASME SA-533 type E. Following additional metallurgical adjustments have been done:

- Low carbon content to meet HAZ hardness requirement of ISO 15156-2;
- Balanced alloying of molybdenum and chromium to achieve tensile properties;
- Addition of Nickel for hardenability and toughness properties. Nickel content is below 1% (weight percent) to be in accordance with current requirements of ISO 15156-2;
- Tramp elements (sulphur, phosphorus, etc.) are kept at very low levels to mitigate the temper embrittlement, and provide sour service properties (e.g. HIC resistance);
- No use of micro-alloying (Nb + V < 0.02%) to ease HAZ softening.

Table below gives the chemical composition as required by ASME code, and the chemistry target for SuperElso® 533E.

mass wt%	C	Mn	Ni	Cr	Mo	S	P
SA-533 type E	≤0.20	1.15-1.70	0.60-1.00	≤0.60	0.25-0.60	≤0.015	≤0.020
SuperElso 533E	≤0.10	1.15-1.70	0.60-1.00	≤0.60	0.25-0.60	≤0.002	≤0.006

Table 2 : heat analysis comparison
(SA-533 type E requirement and SuperElso® 533E)

Industrial applications, manufacture of the vessels and quality procedures

SuperElso® 533E is MnMoNi alloy produced per ASME SA-533 type E class 2 (Yield Strength: 485 MPa min, and Ultimate Tensile Strength: 620 MPa – 795 MPa), and delivered in quenched and tempered condition.
This material targets equipment for which weight reduction is of paramount importance such as slug catchers, separators, amine absorbers or adsorber vessels of the High Pressure gas section. It is even more important for the FLNG units which need to control the weight of topsides. The figure 2 below compares the maximum allowable stresses of SA-533 type E class 2 with carbon steel SA-516 Grade 65, per ASME section VIII division 2 and ASME section II part D, table 5A.

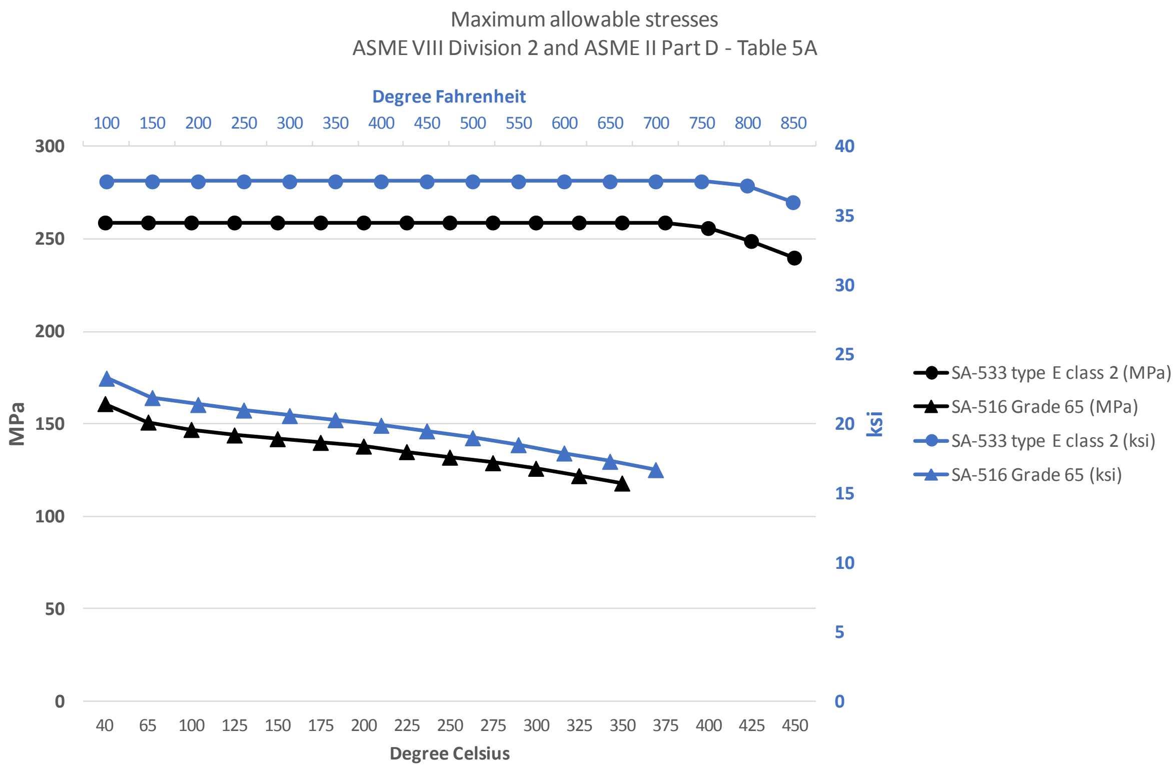


Figure 2 : higher maximum allowable stresses are provided by SA-533 type E class 2

Weldability of SuperElso® 533E has been studied in cooperation with renowned European (ATB Riva Calzoni, Officine Luigi Resta, Midsund Bruk) and Japanese (Hitachi Zosen) fabricators, with insights from Engineering Procurement and Construction companies regarding the target properties.

These studies have been done on 120 mm and 150 mm thick plates using Submerged Arc Welding (SAW) process in flat position (1G) with different types of groove (narrow gap, X type or U type) and different welding consumables. In addition to the evaluation of both tensile and toughness properties, the main objective was to demonstrate the ability of the SuperElso® 533 E material to achieve hardness in Heat Affected Zone (HAZ) below 250 HV10 as required by NACE MR 0175 / ISO 15156-2 standards.
According to ASME BPVC, Post Welding Heat Treatment (PWHT) is mandatory for pressure parts in all thickness for P-number 3 Group 3 which includes SuperElso® 533E material. The minimum required soaking time is 1 hour / 25 mm (1 in.) up to 50 mm (2 in.) plus 15 minutes for each additional 25 mm over 50 mm. The minimum PWHT temperature shall be 595°C as per ASME Section VIII.

In order to cover those requirements and the different possible needs of PWHT during vessel manufacture, several temperature and soaking time of PWHT have been applied.

The effect of heat treatments (tempering, PWHT) on mechanical properties can be determined by the Larson-Miller Parameter (LMP). For several heat treatments, the cumulative effect is given by

$$LMP_{total} = \frac{T_R}{1000} \times \left[20 + \log(t_R + t_{eqi})\right]$$

T_R: Tempering temperature (K)
t_R : Tempering soaking time (h)
t_{eqi} : equivalent soaking time (h) at T_R for a heat treatment initially performed at T_{PWHT} during t_{PWHT}.
T_{PWHT}: PWHT temperature (K)
t_{PWHT}: PWHT soaking time (h)

To determine t_{eqi}, the following equalization equation can be used:

$$LMP_{PWHT} = \frac{T_{PWHT}}{1000} \times [20 + \log(t_{PWHT})] = \frac{T_R}{1000} \times \left[20 + \log(t_{eqi})\right]$$

Charpy V-notch impact tests were done according to ISO 148-1, on samples in transverse orientation (sampling at quarter-thickness) both in base metal and in HAZ. Tests were carried out at temperature between -36°C and -60°C. According to results shown on Figure 3, high impact toughness properties are obtained whatever the LMP value and the tested temperature.

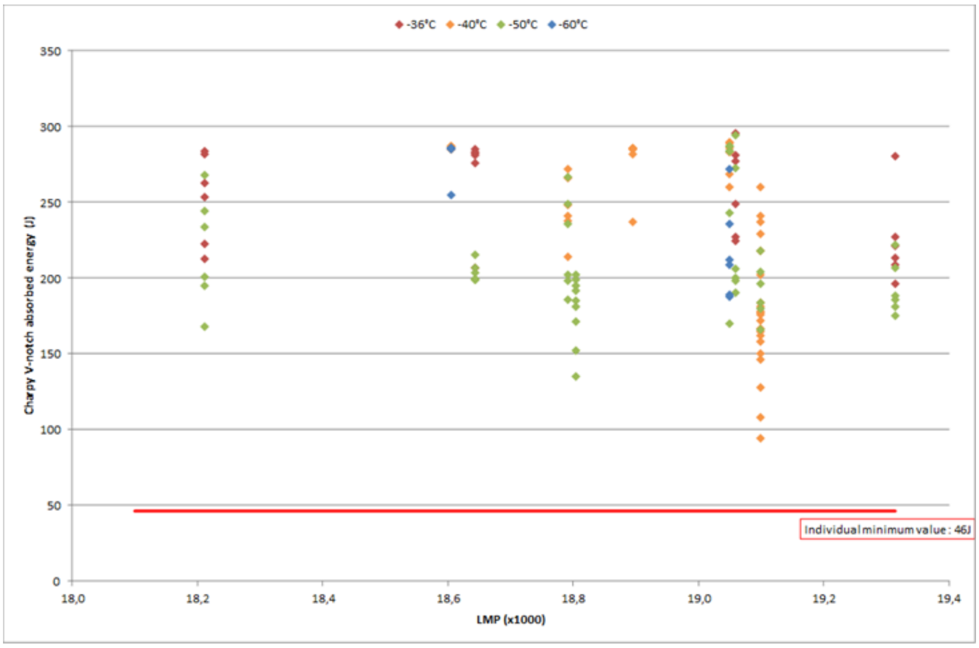


Figure 3 : Charpy-V notch impact toughness depending on LMP (quarter-thickness)

Tensile properties were carried out according to ASME A370, at room temperature in transverse orientation at ½ and ¼ thicknesses. As shown on Figure 4, mechanical properties are in accordance with ASME SA-533 type E class 2.

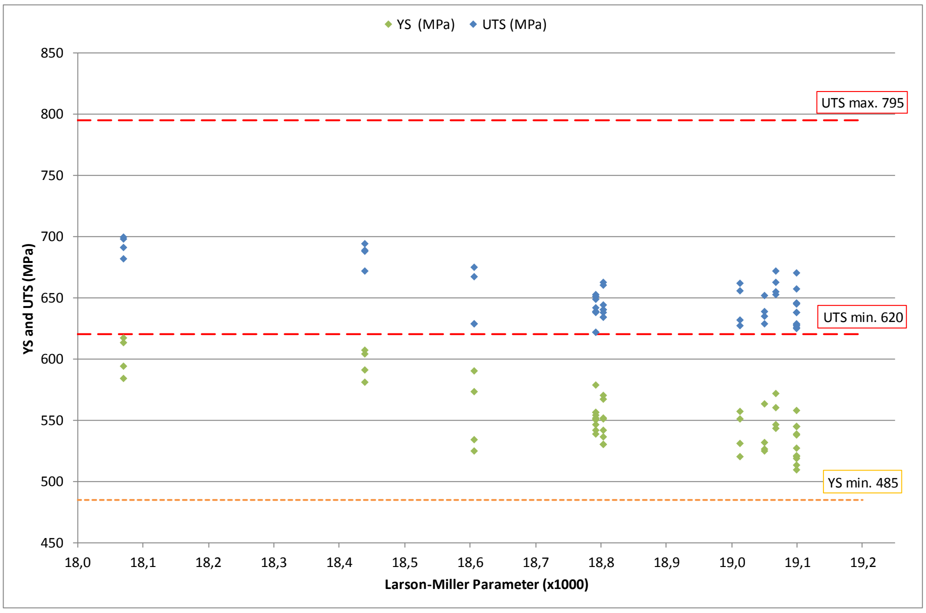


Figure 4 : Transverse yield strength and tensile strength depending on LMP

Vickers Hardness (HV_{10}) testing was realized weld joint cross section following ISO 9015-1. Reading values of hardness have been taken in base metal, heat affected zone and weld metal. All hardness values are presented in Table 3, following PWHT done at 625°C during 5 hours or at 625°C during 15 hours. The appendix 1 details the identification numbers of hardness impressions. Finally, the Figure 5 shows cross welding macrograph and hardness values for a 120 mm thick SAW weld joint after a PWHT at 625°C during 5h.

PWHT	Line	Base metal	HAZ	Coarse grains HAZ	Weld metal	Weld metal	Coarse grains HAZ	HAZ	Base metal
Identification numbers		1 2 3	4 5	6 7 8	9 10 11	12 13 14	15 16 17	18 19	20 21 22
PWHT 625°C / 5h	1.5 mm under top skin	219 211 216	199 234	242 247 249	206 207 202	208 214 208	238 244 249	235 203	220 220 217
	on back gouging	207 199 206	191 214	244 244 232	207 217 222	217 223 226	219 249 228	225 216	199 210 212
	1.5 mm under bottom skin	215 217 218	236 210	236 247 246	226 234 205	199 225 225	248 244 248	239 209	225 225 229
PWHT 625°C / 15h	1.5 mm under top skin	213 209 210	225 199	232 229 236	199 198 196	205 205 202	238 236 234	224 199	215 216 215
	on back gouging	206 204 206	221 197	227 242 238	207 209 215	215 209 207	233 240 233	217 210	198 209 198
	1.5 mm under bottom skin	219 211 217	234 217	241 242 239	219 223 205	204 213 227	235 239 233	231 210	218 220 224

Table 3 - Vickers Hardness results (HV_{10}) on 120 mm thick SAW weld joint after PWHT 625°C/5h

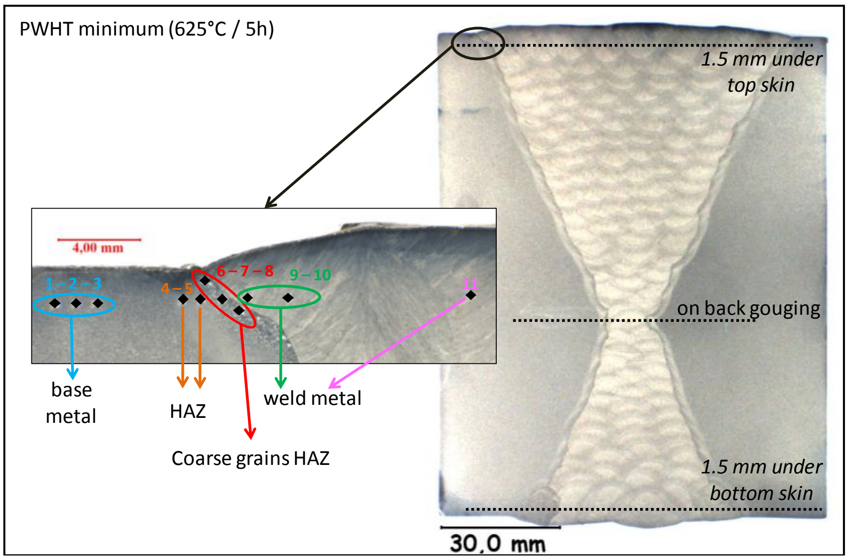


Figure 5 - 120 mm thick Submerged Arc Welding (SAW) cross section macrograph

This macrograph was prepared as following:

- Grinding,
- Automatic polishing with diamond solution (9 µm to 1 µm),
- Etching with Nital 3% etchant (immersion with agitation during 20 sec.),
- Observation with binocular microscope and optical microscope.

No anomaly was detected by microscopic observation. Hardness results are in accordance with standard NACE MR 0175 / ISO 15156-2:2015 with all values being below 250 HV_{10}. For SuperElso® SA-533 Type E, this requirement can be achieved by using an optimized welding process combined with adequate PWHT.

Experimental study

Objectives of the tests on low alloy steels

Although low alloy steels may present some limitations in sweet amine units working at high acid gas loading. They represent the benchmark solution in sour conditions, due to the formation of a more protective iron sulfide scale. Typical grades used for the manufacturing of pressure vessels such as the absorber column consist in HIC resistant SA-516 Gr60 or Gr65. Since pressure is often high in the absorber, there is a real interest in using steel grades with higher strength in order to decrease the thickness of the steel. On the other hand, increasing mechanical properties of low alloy steels often results in higher risks of H2S cracking.
The main objective of the study was thus to compare the behavior of SuperElso® 533E with that of SA-516 Gr65 in terms of corrosion and cracking resistance. Since the main interest of high strength grades lies in weight reduction, absorber conditions were selected.

Test conditions for Carbon steels characterization

Test solution:

Test solution was prepared with analytical grade reagents and deionised water and are representative of EnergizedMDEA (which is a formulated amine made of MDEA plus secondary amines), with a total amine concentration comprised between 40 and 45 % mass. In addition, in order to increase the risks of stress corrosion cracking, chlorides were added in the test solutions at a concentration of 5 g/L. This concentration is far above chloride concentrations usually found in amine units. For the corrosion test on carbon steel samples, only the fresh solution was used, without preliminary degradation phase.

Low alloy steels:

Two steel grades were used for these tests: SA-516 Gr65 as reference, and SuperElso® 533E. The chemical compositions of these two grades are given in Table 4.

	Fe	C	Mn	Si	P	S	Ni	Mo
SA516Gr65	bal.	< 0.2	0.85 – 1.20	0.15 – 0.40	< 0.01	< 0.004	< 0.4	< 0.12
SuperElso® 533E	Bal.	< 0.1	1.15 – 1.70	< 0.40	< 0.007	< 0.002	< 1	0.25 – 0.60

Table 4: Chemical composition (mass %) of carbon steels used for the corrosion tests.

Three types of coupons were used:

- flat coupons for weight-loss corrosion evaluation (60*20*10 mm^3),
- 4 point bend specimens, loaded at 90% of the actual yield strength (120*20*4 mm^3) (figure 6),
- U-bend specimens, allowing to evaluate the impact of plastic deformation (figure 7).

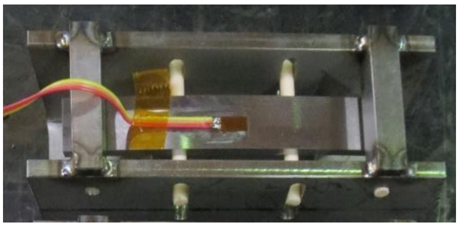


Figure 6: 4 point bend device with strain gauge used during the pre-deformation

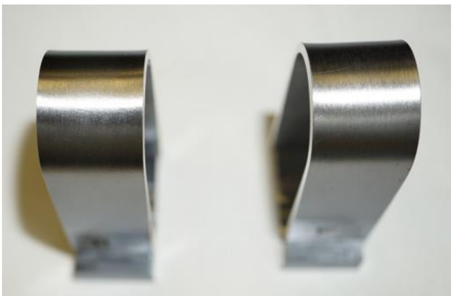


Figure 7: U-bend samples

For each steel grade (SA-516 Gr65 and SuperElso® 533E) two specimens of each type were exposed in the same autoclave (Figure 8).

Figure 8 Samples placed in the autoclave with isolating grid to avoid contact between the samples and the internal surface of the reactor

At the end of the tests, all coupons were rinsed with distilled water and dried. When needed, corrosion scales were removed using a plastic brush and/or by a chemical cleaning method, as proposed in ASTM G1 standard [4]. Weight-loss measurements were then performed on the flat specimens. 4 points bends and U-bend specimens were controlled by visual inspection as well as cross-section examinations to detect the presence of cracks.

Condition of test representative of bottom absorber conditions:

Low alloy steels were exposed in test conditions representative of the absorber in sour gas conditions. Acid gas loading was obtained by contacting a gas mix composed of 15 bar CO_2 and 5 bar H_2S at 95 C, corresponding to $alpha_{CO2}$ = 0.40 mol/mol$_{amine}$; $alpha_{H2S}$ = 0.40 mol/mol$_{lamine}$.
Test duration lasted four weeks and they were maintained in continuous run.

Results

Low alloy steels:

The visual appearance of the samples is shown on Figure 9. There was an homogeneous brown layer on all samples, but no specific corrosion patterns were noticeable (nor localized corrosion, nor crevice near the supports.

a) U-bend samples b) flat coupons c) 4 points bend specimens

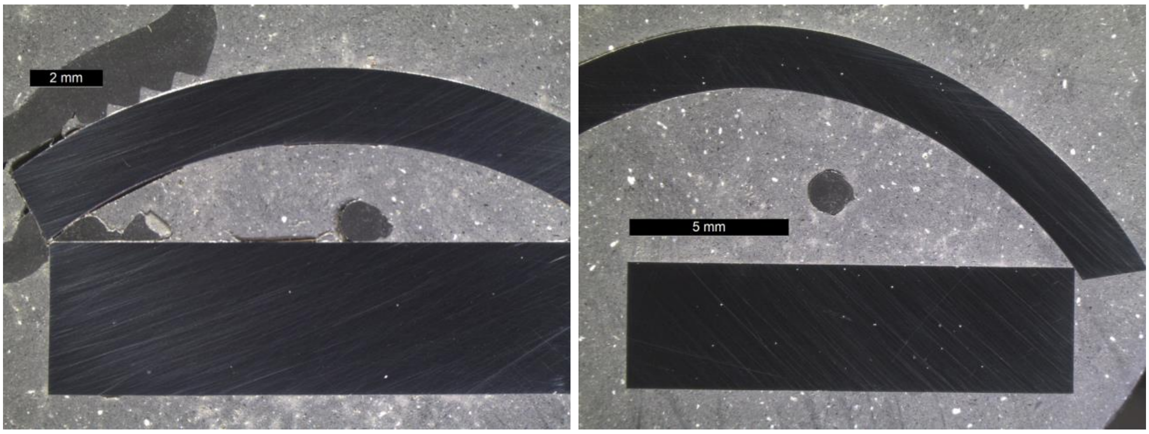
Figure 9: Samples after corrosion test

The corrosion rates measured after the corrosion test are presented in table 5. For both grades, the corrosion rate is very low.

Grade	Rate (µm/year)
SA516Gr65	< 10
SuperElso™ 533E	< 10

Table 5: Corrosion rate after corrosion tests.

The Flexural specimens and U-bend samples were observed on cross-sections to search for cracks. No crack was identified on both grades (Figure 10).



a b

Figure 10 : Cross section of Ubend and 4 points bend samples
a: SA-516 Gr65 ; b : SuperElso® 533E

It has been concluded from these tests that SuperElso® 533E presents similar corrosion and cracking resistance as SA 516 Gr65 steel, so that replacing one grade by the other can be considered. As the codes have confirmed that the material can be used in H_2S and amine service, the last step of the study has checked the economics and validated the interest of the use.

Study of a process case – absorber

The case investigated by the study is an existing unit built in the Middle East. It is a matter of checking the benefits of using nuances of the SuperElso® family on the unit, in the context of a actual project. The approach consists in calculating the weight of the two columns of the AGRU with the alternate materials and comparing them with the steel grades originally selected in the built unit. One can observe the possible gains in terms of steel thickness, which become weight gains and, based on the steel price data provided by Industeel, gains of Capex. The same discussion applies to the construction with Duplex A240 2205 for the regenerator, in the second part of the study.

Bases of calculation

The amine unit processes 380 MMSCFD of gas at 67 bara. The feed gas contains 3.5% H_2S and 5% CO_2 and the solvent flow, consisting of MDEA 45%wt, is 750 Sm3/hr. The absorber is equipped with trays. The regenerator is equipped with trays, with the reflux section. The unit was commissioned in early years after 2000. Tables 6 and 7 describe the unit main parameters.

Gas flowrate	MMSCFD	380
Operating pressure	barg	66
Operating Temperature	°C	91
H_2S content	% mol	4.80
CO_2 content	% mol	5.60

Table 6: main design parameters of the existing unit

		Absorber	**Regenerator**
Dimensions	ID x T/T (m x m)	4.7x 25.8	4.9 x 26.4
Code		ASME VIII div2	ASME VIII div2
Design pressure	barg	75	3.8 +FV
Design Temperature	°C	115	152
Material		SA-516 Gr 65 + clad for top section	SA-516 Gr65 + SS316L clad (3 mm)
Thickness (shell)	mm	127	18
Gross weight (total)	Tons	454	91

Table 7: construction data main design parameters of the existing unit

It is noted that the service imposed by the operating conditions of this AGRU is a "sour" case. As such, steel properties and construction procedures must fulfill NACE MR0175 – ISO 15156-2 requirements [5]. It shall be stated that the use of clad material on SA-516 Gr 65 for the whole regenerator is client's requirement. It goes beyond the Licensor's demand, who normally requests stainless steel in the upper section of the regenerator.

Results

The results are summarized in table 8. The use of the SuperElso® 533E allows a mass gain with an order of magnitude of 35%, bound to the lesser thickness permitted by the high mechanical performances of this steel. The gain in capex is also very interesting, with a difference of - 25% on the price of the supply of material. This discrepancy does not take account of auxiliary costs, such as welding. Indeed, the reduction in the number of welding passes allowed by the reduction of thickness should most certainly balance the additional costs generated by the more restrictive procedures of welding imposed to the SuperElso®.
The weight indicated for the column in table 8 corresponds to the cylindrical section of the shell: the fittings, supports and nozzles, as well as all the reinforcements are not included. The actual weight would be higher than what is reported in the calculation. The study compares only the thickness of the shell.

	Thickness (shell only)	**Weight**	**Cost of material (barrel)**
Reference case : SA-516 Gr65	125 mm	365 tons	512 k$
Alternative metallurgy : SuperElso®533 E Cl2	80 mm	234 tons	375 k$
Savings		35 %	25 %

Table 8 : Estimations of mass and cost of material for the barrel section of the shell of absorber (AGRU Middle East)

The weight gain is very clear for the absorber. The price of the material is higher for the alternative metallurgy and reduces the gain expected on the investment. It is highlighted again that the calculation does not take into account the entire column, in particular the bottom, the nozzles and the brackets.
Table 9 describes the gain for the regenerator.

	Thickness (shell only)	**Calculated weight**	**Material price**
Reference case: SA-516 Gr65	18 mm + Clad SS316L	69 tons	204 k$
Alternate metallurgy: SuperElso® 533 E Cl2	15 mm + Clad SS316L	59 tons	214 k$
Gain (+/-) %		(14.5 %)	5 %

Table 9: Estimations of mass et cost of material for the barrel section of the shell of regenerator (AGRU Middle East)

SuperElso® 533E Steel allows a weight gain even for a low pressure AGRU regenerator column. Nevertheless the price of the material does not translate the gain of weight to net savings on the investment.
It is necessary to mention that any savings of weight generate indirect savings on the transport, the lifting and in general the basement and the civil works needed for the support of the column are not included in the evaluation.

Duplex SA240 2205

Duplex stainless steels were born and have been actively developed by European companies since 1935. Their features make them very attractive compared to equivalent austenitic grades: higher resistance to stress corrosion cracking, higher mechanical properties and lower alloy cost. They are supplied by various mills [6]. They present excellent cost/properties ratios. Today, the SA240 2205 duplex stainless steel is considered as the "work horse" grade.

Characteristics of the steel

The duplex stainless steel SA240 2205 is a material consisting of around 50% of ferrite and 50% of austenite. This phase balance provides this material with excellent corrosion properties and mechanical characteristics. For instance, its yield strength is at least twice the yield strength of conventional austenitic stainless steels such as 316L. It may allow the design engineer to decrease the wall thickness for some pressure vessels applications. Table 10 gives the composition of the steel.

C	Ni	Cr	Mn	Si	Mo	N	Min YS (MPa / *ksi*)	Min UTS (MPa / *ksi*)	E %
- 0.030	4.5 6.5	21.0 23.0	- 2.0	- 1.0	2.5 3.5	0.08 0.20	450 / *65*	620 / *90*	25

Table 10: Chemical composition of SA240 2205 and minimum mechanical properties.

In terms of corrosion resistance, SA240 2205 performs much better than 316L austenitic grade in almost all corrosive media. The most important advantage it that duplex microstructure is known to improve the stress corrosion cracking resistance of stainless steels, which is significantly higher than for standard austenitic grades. Figure 11, for example, compares AISI SS316 and SS304 with SA240 2205.

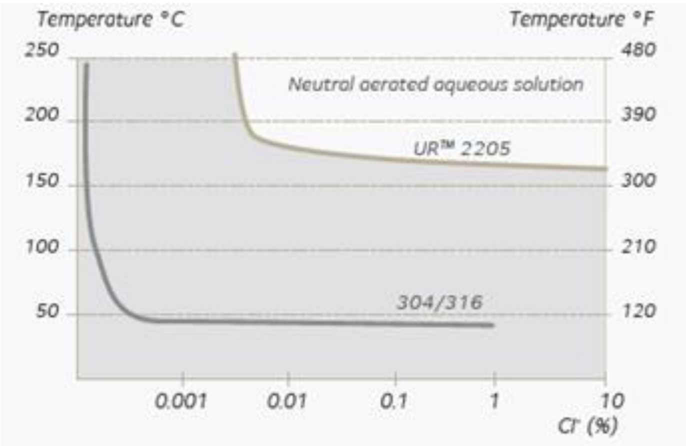


Figure 11: Typical domains of resistance to stress corrosion cracking of austenitic grades and 2205 duplex grade

Industrial applications, manufacture of the vessels and quality procedures

SA240 2205 has been successfully used for decades in various industrial sectors, for example in the oil & gas industry (piping and topside equipment), chemical industry and pulp&paper industry. It can be welded using the most common welding processes (GTAW, GMAW, pulsed GMAW, SMAW, SAW, FCAW, PAW) with a matching filler metal such as 2209 or overalloyed like 2594. There is no need to perform a pre-heating or post-heating treatment. The interpass temperature must be kept below 150°C. The material can be easily welded to carbon steel, with duplex welding consumables.
In the O&G Industry, the family of Duplex stainless steels has been used and some recent publications have presented the feed-back of the operating experience at field [7]. As discussed below, the challenge raised by the presence of H_2S and the actual need to consider possible restrictions for the use of Duplex in sour environment has been also largely evaluated in literature [8].

Experimental study
SA240 2205 has been tested with the same protocol as the SuperElso® 533E presented above. Again the study has started its work with the review of the conditions of application of the steel in sour service and in amine service. The highlights of the review are given below.

Objectives of the tests on corrosion resistant alloys:

Stainless steel grades play an important and increasing part in amine plants. As already presented a few years ago, they offer many advantages in terms of flexibility of the plant, and allow operations at high capacity and high acid gas loadings [9]

As a preamble, it has to be emphasized that AISI 304L and AISI 316L used for internal claddings, heat exchangers and piping have proved a complete long term success based on 30 to 40 years' experience. However, usual standards for oil and gas production in sour environment point out the risks of environmental cracking of CRAs. Indeed, NACE MR0175/ISO 15156-3 [10] gives requirements and recommendations for the selection and qualification of CRAs for equipment used in oil and gas production and in natural gas treatment plants in H_2S containing environments. Table A.2 of the standard gives the environmental and materials limits applicable to the usual austenitic stainless steel grades for any equipment or components. It is particularly stated that grades such as 316L shall not withstand H_2S partial pressure above 1 bar (15 psi), for a maximum temperature of 60 °C (140 °F). For higher H_2S partial pressure (up to 3.5 bar), the maximum recommended chloride concentration is 50 mg/L. Similarly, Table A.24 of ISO 15156-3 gives environmental limits for duplex steels. According to this document, 2205 grade shall not be used above 232 °C (450 °F) and 0.1 bar (1.5 psi) H_2S. These limits are summarized in Table 11.

Materials type	T° (max)	P_{H2S} (max)	Chloride (max)	Remarks
Austenitic grades such as 316L	60 °C	1 bar	Cf. remark	Any combinations of chloride concentration and *in situ* pH occurring in production environments are acceptable
	60 °C	3.5 bar	50 mg/L	*In situ* pH values occurring in production environments are acceptable.
Duplex grades with 30 < PREN < 40 and Mo > 1.5 %	232 °C	0.1 bar	Cf. remark	Any combinations of chloride concentration and *in situ* pH occurring in production environments are acceptable

Table 11: Environmental and materials limits for austenitic and duplex stainless steels used for any equipment or component, according to NACE MR0175 / ISO 15156-3 (extracts from Table A.2 and A24) [10]

Considering that the pressure of the acid gas stream at the inlet of an amine plant is typically around 70 bar, 0.1 bar PH_2S corresponds to 0.14 vol. %, and PH_2S = 3.5 bar corresponds to 5% H_2S. Many of the sour gas treating units are therefore far beyond these levels. A strict application of the standard would thus require strong limitations for the use of both austenitic and duplex stainless steel grades in amine plants. However, even though these limitations are well documented and approved by the oil and gas actors, it must be noted that ISO 15156 is intended to be used for oil and gas production environments consisting mainly of acid brines with CO_2 and H_2S. This definition does not apply to amine solutions, which present typical pH ranging from 8 to 11. Consequently, it looks that amine plants present a less severe environment towards cracking of CRAs. Indeed, the overall reported experience is very positive with standard austenitic stainless steels. From our own experience on existing units and also from literature [11]-[12]-[13], no significant cracking problems were reported up to 4 – 6 g/L chlorides. Additionally, laboratory studies conducted in the late 90's by Total demonstrated a total absence of SCC of 316L and 304L. More recently, other tests were repeated at IFPEN: 304L and 316L U-bends specimens were exposed at 110°C to 40% MDEA with a 0.6 Mol/Mol sour gas loading and up to 10 g/L NaCl (6 g/L chloride). After one month, the specimen were examined and revealed a complete absence of pits or cracks. Table 12 summarizes the successful laboratory tests of austenitic stainless steel in conditions of sour amine units.

Amine	Gas loading	T°	Cl^-	Steel type	Result	Reference
DEA 4N	10 bar H_2S + 7 bar CO_2	110°C	6 g/L	AISI 321	No cracking-No pitting	Total internal report
MDEA 40%	4.7 bar H_2S + 1.8 bar CO_2	110°C	6 g/L	AISI 304L AISI 316L	No cracking-No pitting No cracking-No pitting	IFPEN internal report
MDEA 50%		98°C	10 g/L	AISI 316L AISI 304L AISI 410	No pitting No pitting No pitting	[11] to [13]

Table 12: Austenitic stainless steel laboratory test results in sour amine units conditions

Industrial experience of duplex stainless steels in amine service is not as documented. However, according to API 938-C [14] dealing with the use of duplex stainless steels in oil refining applications including refinery amine units, ‘’refining environments have significant differences in pH, other contaminants, etc., and hence, the NACE MR0175 limits are not always applicable. Refining applications of duplex stainless steels have often exceeded, and

sometimes significantly, the H_2S partial pressure limits in NACE MR0175, and the duplex stainless steels have proven good resistance‘’.
It can be concluded from these experiences that AISI 316L or duplex stainless steels can be used in sour amine units even in presence of chlorides far beyond the 50 mg/L recommended by the NACE MR0175/ISO 15156-3 standard or at H_2S partial pressure above 0.1 bar. In order to confirm these claims, the main objective of this study is to verify the absence of SSC / SCC for 316L and duplex 2205 exposed to amine solvent at 120°C and at 0.5 bar H_2S and 5 g/L dissolved chlorides.

Test conditions for Duplex characterization

Test solutions:

Test solutions were prepared with analytical grade reagents and deionised water and are representative of EnergizedMDEA[1], with a total amine concentration comprised between 40 and 45 % mass. In addition, in order to increase the risks of stress corrosion cracking, chlorides were added in the test solutions at a concentration of 5 g/L. This concentration is far above chloride concentrations usually found in amine units.
Two kinds of solution were used: one freshly prepared, and the other which was preliminary degraded. This degradation step consisted in 14 days exposure of the test solution at high-temperature (140°C) under 40 bar CO_2 loading with 60 g of iron filing added in the reactor, allowing reaching 1 mL of test solution for 1 cm² of exposed iron. Since dissolved iron participates in the degradation of amines, this procedure tends to reproduce natural degradation in real service, leading to the formation of potentially more corrosive species. This degraded solution was then filtered through 3 µm membrane. Validation of the efficiency of this procedure was published elsewhere [2]
These test solutions were then used for samples exposures in a 5L autoclave made of Hastelloy C276. The picture of the test set-up is available on figure 12.

Figure 12 Autoclave for corrosion test

[1] EnergizedMDEA is the trade name of formulated amine from the Advamine™ portfolio.

Corrosion resistant alloys:

Two stainless steel grades were used for these tests: 316L as reference, and Duplex 2205. The chemical compositions of these two grades are given in table 13.

	C	Cr	Ni	Mn	Si	P	S	Mo	N
316L	0.03	16-18	10-14	2	1	0.045	0.03	2-3	0.1
2205	0.03	21-23	4.5-6.5	2	1	0.03	0.02	2.5-3.5	0.08-0.2

Table 13: Chemical composition (wt. %) of stainless steels used for the corrosion tests.

Two types of coupons were used:
- flat coupons for weight-loss corrosion evaluation (60*20*10 mm^3),
- U-bend specimens with welded zone, allowing to evaluate the impact of plastic deformation and the impact of welding (120*20*4 mm^3).

These coupons were machined from thick plates, representative of industrial products used for the manufacturing of pressure vessels. For each steel grade (316L and duplex 2205), two specimens of each type were exposed in the same autoclave.
At the end of the tests, all coupons were rinsed with distilled water and dried. When needed, corrosion scales were removed using a plastic brush and/or by a chemical cleaning method, as proposed in ASTM G1 standard [4]. Weight-loss measurements were then performed on the flat specimens. U-bend specimens were controlled by visual inspection as well as cross-section examinations to detect the presence of cracks.

Condition of test representative of regenerator entry:

Stainless steel grades were exposed in test conditions representative of the top of the regenerator in sour gas conditions. Acid gas loading was obtained by contacting a gas mix at 45 bar, composed of N2 + 10% CO2 and 1 % H2S at 120 °C, corresponding to $alpha_{CO2}$ = 0.26 mol/mol_{amine}; $alpha_{H2S}$ = 0.08 mol/mol_{lamine}. The duration of the tests was 4 weeks, without interruption.

Results

The corrosion rates measured after the tests in freshly prepared solution, and in degraded solution are presented in table 14. For both stainless steel grades, no corrosion was detected by this method.

Grade	Fresh solution	Degraded solution
AISI 316L	< 5	< 5
Duplex 2205	< 5	< 5

Table 14: Corrosion rate (µm/year) after corrosion tests.

The samples were observed with an optical microscope. No indication of localized corrosion was detected, and the cross section of U-bend samples did not reveal any crack (Figure 13: and Figure 14).

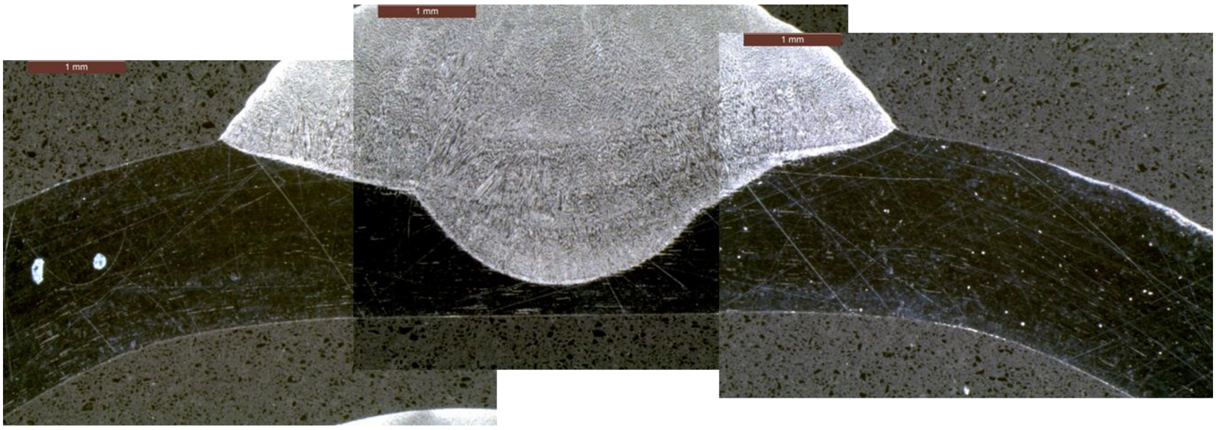


Figure 13: Cross section of weld on U-bend on SS316L

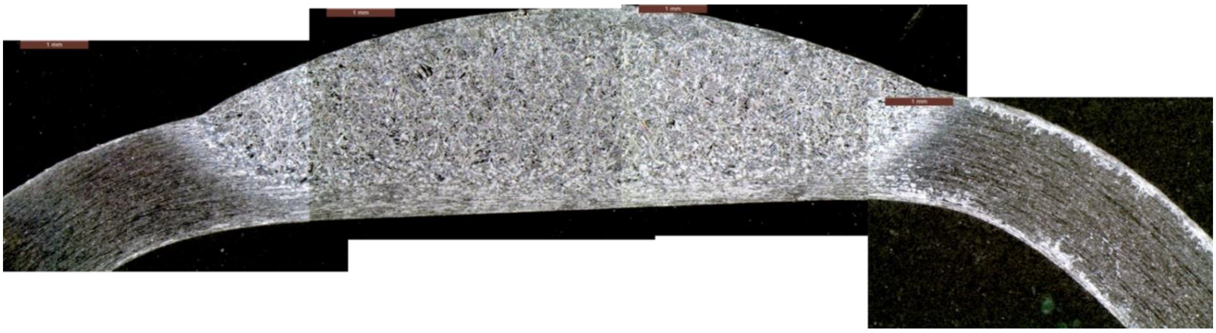


Figure 14: Cross section of weld on U-bend on Duplex 2205

It can be concluded from these tests that duplex 2205 is a good alternative to 316L for amine service with sour gases, even beyond the 0.1 bar H_2S limit given in NACE MR 0175 – ISO 15156-3.

<u>Application to a process case of AGRU – Regenerator</u>

In order to check the interest to use Duplex for the construction of the vessels of gas treatment units, the application case study has focused on the same case as the one investigated for the benefits of SA-533 Type E (see the bases of design given above). Again the evaluation has been completed in collaboration with INDUSTEEL. It looks at the regenerator because the use of plain duplex for the absorber is considered as too expensive for this case. Duplex can however be a solution for offshore and marine applications because of its resistance to the sour atmosphere. The evaluation of a specific offshore case is not part of this study.

The reference design uses a carbon steel type SA-516 grade 65 fully clad with SS316L (3 mm clad). It is compared to a case using solid duplex SA-240 2205 stainless steel.

The calculation and comparisons were conducted directly by Industeel, using the ASME BPVC, Section VIII Division 2 calculation code. The code is identical for any grades of steel. The early calculation considers the effect of pressure. The use of duplex SA-240 2205 allows a decrease in thickness of almost 40% compared to the steel SA-516 Gr65 (see table 14). However, it is highlighted that the calculations of thicknesses given herepresented below are preliminary because they have been made by taking into account only the influence of the internal pressure. So are excluded from the bases of calculation (and for the comparison), the rigidity of the self-supporting vertical tower, the influence of the weight of the internals added to the column, like nozzles and manholes, the heads, the external supports and clips, and all the other sort of constraints imposed to the structure (resistance to seismic efforts, to the efforts resulting from connections on nozzles, of stiffness, of wind etc...). The simplification has lead to figures of thickness largely underestimated compared to the actual design. For example, using the reference steel SA-516 Gr65, the actual column had a thickness of 18 mm, when the calculation results in a thickness of 5.7 mm. The gain is applied to the thickness of the barrel section of the shell of the existing column, around 2.5 mm, and is shown in table 15.

	Thickness (shell only) / mm
Reference material SA-516 Gr65 (unclad)	5.7
Alternate with Duplex SA240 2205	3.3
Saving	**(42%)**

Table 15: Comparison of wall thicknesses according to the metallurgy used for a regenerative column (code ASME VIII-2, corrosion thickness 0 mm, pressure and design temperature of 3.8 bar and 152 °C).

On the other hand, the mass and cost calculations have had to be made on a more realistic basis, considering the actual thickness of the tower of the as-built case (18 mm + 3 mm cladding in SS316L). The use of Duplex enables a reduced thickness of 25% for the solid Duplex solution (which gives 15 mm). A third case, implementing a low alloy steel type SuperElso® 533 E Cl2 (15 mm, again + 3 mm clad of AISI 316L as needed for CS based material in this regeneration service) is also recalled for comparison. The study highlights the calculation of thickness with SuperElso® 533 E Cl2 is almost the same as the one with Duplex (clad excluded).
The cost comparison between the various solutions has been carried out on the basis of the cost of supply of the plates of steel by INDUSTEEL (EXW) at the time of the study. Again the study is restrictive, as only the costs of the supply of material have been taken into account. It excludes the engineering costs, the fabrication, the transport, the welding, or any QA/QC or stamping costs. For the calculation and comparison of masses, only the straight section of shell (height 26.4 m) is considered. The heads are not included.

The overall results of these calculations are presented in table 16. The use of duplex 2205 allows a net gain of 25% for the mass of the shell: it is, linked on one side to the lesser thickness permitted by the best mechanical qualities of this steel, combined with the absence of cladded steel in 316L. The clad is added to the total mass but does not participate to the structural mechanics of the whole. The gain in Capex keeps it fairly interesting, with a cut difference of 22.5 % on the price of material supply. This discrepancy, which may surprise any the user of "noble" metallurgy in place of a carbon steel solution, is due to the significant additional cost associated to the cladding of low thickness CS plates.

	Thickness (shell only)	**Calculated weight**	**Material price**
Base case SA-516 Gr65	18 mm + clad	69 tons	204 k$
Alternate Duplex SA240 2205	15.5mm	52 tons	166 k$
Saving (Duplex / SA-516 Gr65 + clad)		**(25%)**	**(22.5 %)**
Alternate metallurgy: SuperElso® 533 E Cl2	15 mm + clad	59 tons	214 k$

Table 16: Estimation of weight and investment costs based on the price of the raw material (shell of the regenerator).

It is also highlighted that the use of plain Duplex is more attractive than SuperElso®, because of the need to clad the low alloy steel similarly to SA-516 Gr65.

Even for equipment operating at low pressure, there is an interest to use Duplex steel. The gains are obvious in terms of weight. Coming to the investment part, the table shows again a gain, both due to the saving of weight but also to the comparison with a clad material which is expensive. However, the gain has to be balanced by the more costly management of Duplex steel as a construction material. The use of Duplex steel is more expensive because:

- Forged parts are usually more expensive
- Welding is more delicate
- The manufacturing requires qualified workshops. There are not so many players. The reduced competition does not allow to levered the prices

The savings would have to be balanced by the consideration to the elements given above. On the contrary, the weight cuts provided by a Duplex column would be enforced by additional savings on all the weight-dependent operations for and around the tower: transport, foundations, supports and matters relative to civil works, and finally lifting.

Finally, it is pointed out that equipment made out with Duplex SA240 2205 steel do not usually require painting in harsh conditions. These steels are used very commonly in offshore and marine conditions, while the CS and SS316L require treatments of their external surface, which can be potentially expensive and time consuming (especially for stainless steel). This is another source of benefits that can be considered by the use of duplex steel.

Conclusions

The acid gas removal units of natural gas treatments usually feature heavy weight towers, mainly on the high pressure part. PROSERNAT, IFPEN and INDUSTEEL have jointly investigated the possibility of alternate materials to reduce the weight of major equipment in amine based AGRU's.
The current work has assessed the use of Duplex SA240 2205 stainless steel and SuperElso® 533 E low alloy steel for their application in gas treatment units using amine solvents. Several criteria and tests were included in the study.
SuperElso®533 E is a low alloy steel which can be delivered with a HIC grade and comply with the NACE MR0175 / ISO-15156-2 requirements for carbon steels.
The study has included an extensive review of the standards applicable in the oil and gas industry documents and reference codes of the profession. It has showed that there were no barriers to the use of the Duplex steels in the presence of liquid solutions amines of gas treatment, even in H_2S conditions. Indeed, the alkaline pH of these solutions radically deviates from the conditions of exploration – oil production (acidic pH in the case of water condensation without pH buffering amine), for which certain instructions (notably NACE MR0175/ISO ISO-15156-3) impose restrictions on the use of Duplexes as soon as the H_2S content exceeds 0.1 bar.
Two experimental tests were then carried out in an amine solution, in conditions representative of the regeneration and solvent loaded with CO_2 and H_2S. These tests showed that in the same way as austenitic 316L stainless steel, widely used in amine units, the 2205 Duplex steel had very good corrosion resistance (velocity less than 1 µm/yr). The tests under constraints (U-bend coupons) confirmed the resistance to corrosion, even in the presence of contents of chlorides higher than the usual recommendations.
The study has also included an economic comparison completed with the support of INDUSTEEL. The practical study has evaluated the benefits of alternate materials for the absorber and the regenerator of an amine unit, currently in operation and originally built in carbon steel or carbon steel cladded with stainless steel SS316L.
The underlying service conditions of the 127 mm thick SA-516 Gr65 absorber are imposed by an amine solvent enriched with H_2S and CO_2 at 85 °C. The use of low alloy steel with high mechanical properties allows a reduction in thickness (and mass) of 35% for the shell which means a cost reduction of 25% on the material for the shell.
The use of massive 2205 duplex steel allows a mass reduction of 25% of the regenerator cylinder part. The significant gain can be a very attractive asset for conventional applications, but even more for offshore applications where mass gains are particularly sought, in replacement of carbon and SS 316L steels which impose expensive external surface protections.

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Appendix 1: Identification numbers of hardness impressions

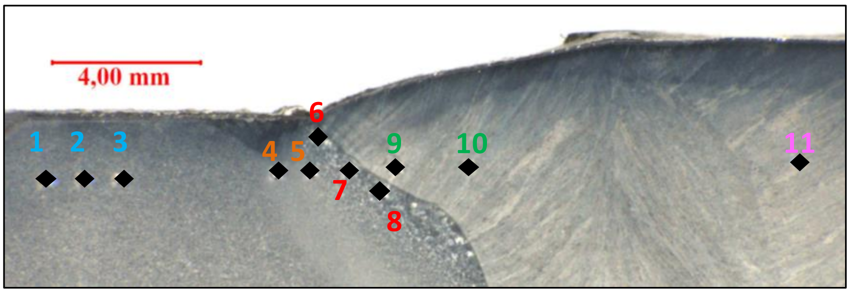

Figure A1:"1.5 mm under top skin" line

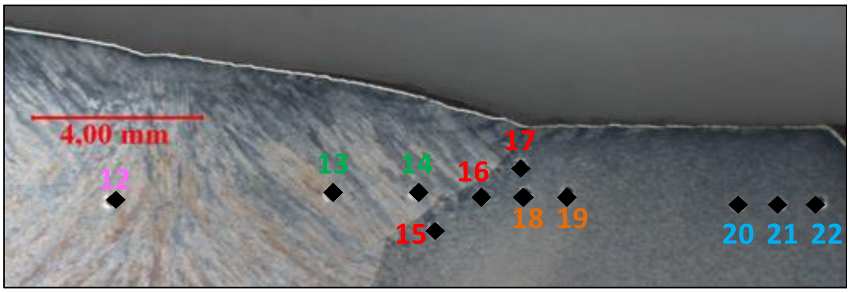

Figure A2: "1.5 mm under top skin" line (cont'd)

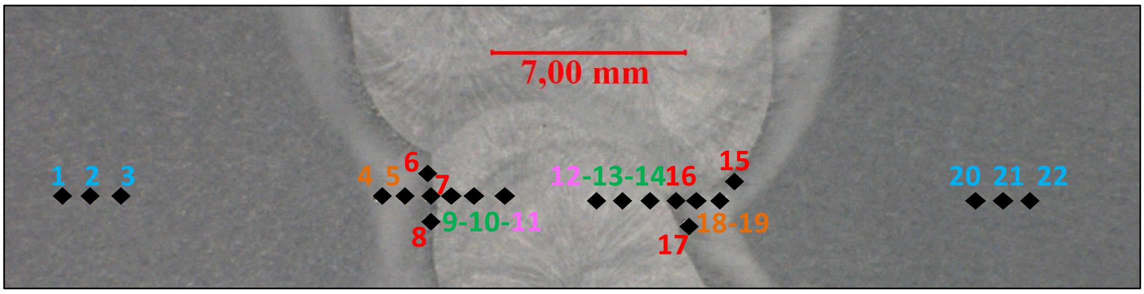

Figure A3: "on back gouging" line

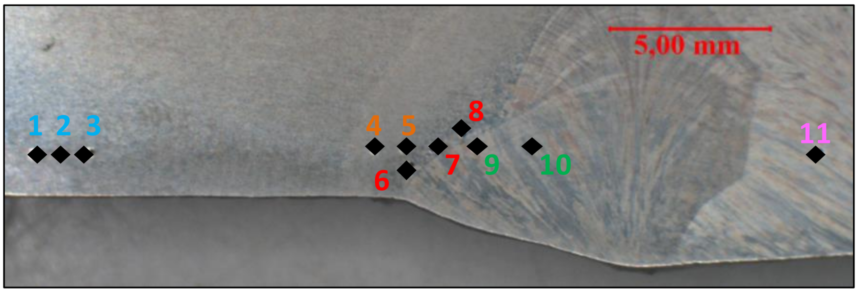

Figure A4: 1.5 mm under bottom skin" line

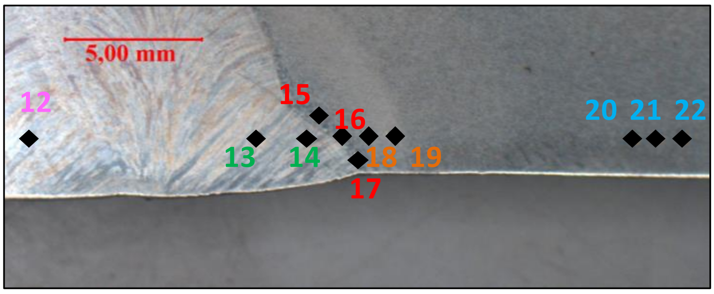

Figure A5: "1.5 mm under bottom skin" line (cont'd)