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MATERIAL SELECTION AND CORROSION RESISTANT ALLOYS FOR PETROLEUM INDUSTRY

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ABSTRACT
Oil and gas production has been a subject intensively emphasized during the last decade, due to its magnitude on our daily life. Invaluable amount of money is being constantly invested worldwide for research into this non-renewable resource, especially on technology and materials. For this reason, the present article aims to bring an approach to material selection for subsea, topside and down hole rigs, taking into consideration the major challenges for each side.
By pointing out the major particularities of inconel, super duplex, hastelloy and their cheaper alternatives, engineers willing to deepen the material science for petroleum industry will be having a good starting point. Another aspect that has been linked to the study concerns the corrosion control of production systems. Starting with the evaluation of the parameters that affect the process, the paper states some basic measures for counteracting this destructive phenomena. Considering that all products in this branch of technology are operating under heavy duty and need to have long warranty, the authors perspective conveys the most innovative materials, almost unaffordable for batch production in other industries.
Keywords: Material selection, petroleum industry, corrosion.

1. INTRODUCTION

Basically, selection relies especially on robust materials, with limited need for inspection and maintenance. The most appropriate choice deppendsmostlyon the environment, operating pressure, temperature and destination.
Topside branch has serious challenges in meeting the EU requirements for operating at large temperature variations (from -20 C to 130 oC) and pressure up to 50 MPa [1]. Also, it is supposed to resist at high nozzle forces and moments, given by end connections to upstream and downstream pipes.
Down hole equipment is subjected to exploitation under extremely high temperature (up to 225 o C) and a differential pressure (inside/outside) of 140 MPa.
For the Subsea field, the external conditions usuallyimply a depth between 750 and 1500m below sea water, where pressure ranges from 20 to 180 bar. More than that, 92% of the sea floor has a temperature laying between 1.5 o C and 4.5 o C [2]. Speaking of the operating conditions, these are more severe: -40 oC to 150 oC temperature and 35 MPa design pressure.

2. MATERIAL CLASSIFICATION

First of all, it is important to understand the role of the principal constitutive components of an alloy: iron reduces material cost and controls thermal expansion; copper provides resistance to reducing acids (phosphoric, sulfuric and hydrochloric); chromium increases high temperature strength and

resistance to oxidation and sulfidation; nickel improves metallurgical stability, weldability and resistance to stress corrosion; aluminum speeds up age hardening and resistance to oxidation at elevated temperatures; titanium enhances age hardening and decreases the total weight; molybdenum contributes to high temperature strength and reduces acids; niobium increases resistance to pitting and crevice corrosion; tungsten renders to a better weldability and strength; cobalt makes the alloy resistant to carburization and sulfidation; nitrogen offes metallurgical stability and strength.
The expenses for obtaining quality alloys are in direct ratio to the performance desired. More than that, a material selection leads to a material solution and all factors must be accounted for national regulations, international standards, operational experience, previous products, etc. Usually, carbon steel shall normally be selected for all systems unless it can be demonstrated that corrosion resistant alloys are more effective, saving important financial resources. As low cost alternatives, are to be mentioned low alloyed stainless steels in combination with protective painting, carbon steel with polymer materials or pipe-in-pipe solutions for hydrate control.
According to standards, materials in the oil and gas industry have been divided into five categories.

2.1 Carbon Steel Alloys are mainly used for lifting equipment, pressure vessels, valves, drains and tanks. Mindfulness attention is to be given to ultra-high category (max 2% carbon in composition), known for high hardness and manufactured by using powder metallurgy.

2.2 Titanium Alloys represent an outstanding choice for seawater applications, having a unique combination of mechanical and physical properties. With a high structural efficiency and low density (half of the weight of steel and nickel) it is desirable for critical oil and gas equipment. It is generally resistant to stress corrosion cracking and corrosion fatigue, enduring in environments with temperature up to 315 oC [3].
While unalloyed titanium has grades from one to four, the ones used for tubing and welded pipes are classified from five: grade 5 (the most commercially available), grade 7 (the most resistant to corrosion), grade 11 (excellent weldability), grade 16 (low cost), grade 19 (optimal for hydrocarbon production, drilling).

2.3 Stainless Steel Alloys have a ferrites structure, combined with minimum 11% chromium, nickel, manganese and other elements [4]. The fundamental feature of duplex stainless steel is their dual phase microstructure, 50% austenitic and 50% ferrites, that comprises high strength (515 – 930 MPa) and corrosion resistance. For better performance, super duplex class has an addition of chromium, tungsten and copper, offering a better pitting and crevice rusting resistance.

2.4Martensitic Stainless Steel class has been designed for corrosion resistance and hardenable by heat treatment, containing iron, chromium and carbon, with no nickel. In comparison with austenitic stainless steel, this material can be subdued to non destructive testing, by using magnetic particle inspection method. For petroleum field, it is used for bolts, nuts and screws, exposed to shear and tensile stress.

2.5 Nickel alloys are used in a wide range of applications, including petrochemical processing, marine engineering, oil and gas extraction, piping, valves exposed to high temperature, due to their excellent corrosion resistance and good mechanical properties. The most popular alloy in this class is Inconel, used especially for its behavior in extreme conditions. Incolloy is ideal for building process pipes and valves, sensitive from the chemical point of view. Then, Monel is very difficult to machine and needs to be insulated from other metals, such as steel. Hastelloy, the superlative in this field, is patented with localized corrosion resistance better than Inconel, often used in flue gas desulfurization equipment.Details concerning some of the alloys being studied are listed in Table 1 [3,4,5,6,7].

Table 1.Principal alloys used in the oil and gas industry

Material type	Grade	Standard	Composition
Carbon Steel Alloys	A ST 52	DIN 17135	C, 0.3% Cr, 0.3% Cu, 0.5% Ni, 0.03% Ti, 0.1% V,0.08% Mo, 0.005 Nb
	A 516 Gr. 70	ASME SA 516	Max 0.27% C; 1.20% Mn, 0.4% Si 0.035% P, 0.035% S
	5L X-70	ASTM API 5L	0.3% C, 1.33% Mn, 0.28% Cu, 0.28% Cr, 0.18% Si, 0.16%Ni
Titanium Alloys	Gr.5 (UNS N56400)	ASTM B862-09	6% Al, 4% V, 0.25% Fe, remaining Ti
	Gr. 7	ASTM B862-09	99% Ti, 0.25% Pd, C, Fe, N, H
	Gr. 19	ASTM B862-09	8% V, 6% Cr, 4% Zr, 4% Mo, 3% Al
Stainless Steel Alloys	22 Cr Duplex (UNS S31803)	ASTM A 240	22% Cr, 5.5% Ni, 3% Mo, 0.17% N, 0.02% C
	25 Cr Super Duplex (UNS 32760)	ASTM A 276	25% Cr, 7% Ni, 3.5% Mo, 0.6% W, 0.5% Cu, 0.25% N, 0.03% C
	316L Austenitic (S21600)	ASTM A240	16.3% Cr, 10.1% Ni, 2.1% Mo, 0.07% N, 0.02% C
Martensitic Stainless Steel	UNS S41000	ASTM A276	Fe, 13.5% Cr, 0.15% C, <1% Mn, <1% Si, <0.04% P, <0.03% S
	UNS S41600	ASTM A582	Fe, 14.0% Cr, <1.25% Mn, <1.0% Si, >0.15% S, <0.15% C, <0.06% P
	UNS S43100	ASTM A276	Fe, 17% Cr, 2.5% Ni, <1% Mn, <1% Si, <0.2% C, <0.04% P, <0.03% S
Nickel alloys	Inconel 625 (UNS N06625)	ASTM B446	58% Ni, 21.5% Cr, 9% Mo, 2.5% Fe, 3.6% Nb
	Incoloy 825 (UNS N08825)	ASTM B163	42% Ni, 21.5% Cr, 3% Mo, 28% Fe, 2% Cu
	Monel 400 (UNS N04400)	ASTM B127	63% Ni, 34% Cu, 2.5% Fe, 2% Mn, 0.3% C
	Hastelloy G-30	ASTM B366	43% Ni, 31.5% Cr, 15% Fe, 6% Mo, 5% Co, 4% W, 1.5% Mn

3. TYPES OF CORROSION

Being the most important parameter to worsen the quality of materials in the oil and gas industry, corrosion must be carefully kept under control. In addition to the existing study this section will describe particular cases, so that people working in this field to be aware of the causes and perform advised actions.

3.1 General Corrosion represents the most common metal destruction, asserting as a uniform attack over the entire surface area. The chemical reaction that occurs uniformly reduces the thickness, resulting in perforating the material layer after layer.

3.2 Localized Corrosion appears in a very specific zone on the affected face, taking several forms: pitting, crevice attack and microbially influenced corrosion.
Pitting attack results in the formation of holes in metal. Even if small-sized, they can propagate easily and perforate the material rapidly. The micro environment can be autocatalytic, leading to a very aggressive form of corrosion [9].
Crevice corrosion appears in a completely sealed slot between two surfaces (gaskets or fasteners). Depending on material density, the destructive process can move very quickly.

3.3 Environmentally Assisted Cracking is performed under two conditions: chemical reactions in the environment and mechanical condition of the metal itself. Such type of processes are: stress corrosion cracking (presence of tensile stress and a corrosive medium), liquid metal cracking (metal is cracked by a low melting liquid metal), hydrogen embrittlement (surface is penetrated by elemental hydrogen) and corrosion fatigue. Erosion Corrosion consists in the acceleration of metal destruction, due to a relative movement between the corrosive environment and material surface. As a result, layers to be cast out is made similar to dissolved ions, mechanically set asside. Dealloying represents the selective removal of one element of an alloy, arrear to corrosion process (eg. selective removal of zinc from brass, dezincification).For a better understanding of the above mentioned particular cases, figure 1 will present the principal types of corrosion [8].

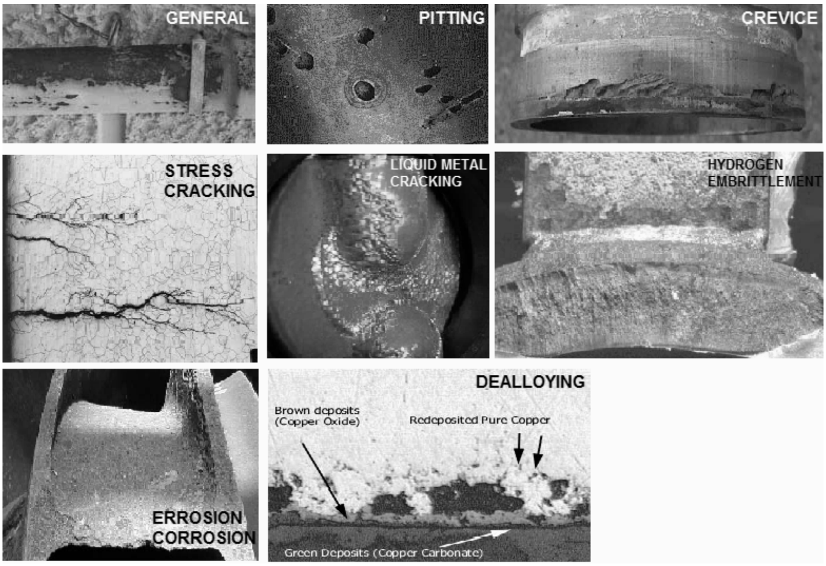

Figure 1. Main types of corrosion effects [photo courtesy of Johnsen R., NTNU]

4. CONCLUDING REMARKS

Key parameters for the proper selection of alloys in the petroleum field have been stated, the table comprising the basic materials for each category. For cost reduction, keep in mind that carbon steel should be taken as a base case. While identifying the danger of corrosion occurrence, change the material quality as high as possible to counteract destruction. For the future, the authors interest will be asserted to materials study, considering that development of better alloys will bring outstanding performance worldwide.

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