

Preliminary Assessment of 22Cr and 15Cr Materials Selection for CO₂ Enhanced Oil Recovery Program

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Abstract. Enhanced Oil Recovery (EOR) program to increase oil production from mature fields are now being implemented in Indonesia amid concern over the continuous decrease of oil production level. The mature fields and EOR process have the tendency to carry relatively high impurities components (CO₂, H₂S, chloride ions) that results in early corrosion occurrence, creating damages in the subsurface equipment (wellhead, tubing, Xmas tree, etc). In Java area with 0.09 TSCF potential gas reserves, 49.3 MMSTB oil and $\pm 23\%$ CO₂ content, such amount of CO₂ gas and possibility of H₂S and chloride from the reservoir will require a higher grade material than the conventional carbon steel. This paper discuss the preliminary materials selection process in the program plan based on the existing condition. The material selection based on the evaluation of closest field data, literature review as a comparison, material, and fluid analysis test. Duplex 22Cr-15 Cr materials are the main study in the paper as the candidate for the tubing material in high CO₂, high H₂S and chloride environment. The polarization result in 27°C and 50°C showed that the chrome 22 %Cr material had pitting tendency in chloride ion 25,000 ppm, while at high temperature (80 °C) the pitting tendency shifted to 5,000 ppm of chloride ion.

1 Introduction

Indonesia's oil production is experiencing production deflation down to around 800 thousand barrels per day and based on data from Indonesia's Ministry of Energy and Mineral Resources, it is mentioned that unrecoverable resources substitution potential have reached 46.42 billion STB, of which are EOR method in the amount of 4.3 billion STB and potential pilot project CO₂ Flooding EOR Project in Java with 0.09 TSCF potential gas reserves, oil is 29.3 MMSTB and $\pm 23\%$ CO₂ content [1]. One of the oil lifting methods with EOR is injecting CO₂ into future production's formation candidate and CO₂ gas source can be extracted from its vicinity. Few of Indonesia's gas fields which are owned by PERTAMINA contain CO₂ components that can be used for oil lifting using CO₂ EOR method [2].

The existence of H₂S, CO₂ and chloride ions are less favored due to a corrosion issue. Lifting activities and transporting oil and gas will transport impurities (H₂S, CO₂ and chloride ions) which impact on corrosive/material degradation on metal-based material surfaces that eventually will stop the production activity, loss of income and equipment's reliability problems. Material degradation or commonly mentioned as corrosion, which is 60% material failure [3-4] in oil and gas fields, is caused by CO₂ corrosion.

In oil and gas production's environment, there are few components in oil and gas fluids that are corrosive in nature, which are oxygen - O₂ (oxygen attack), carbon dioxide - CO₂ (sweet corrosion), hydrogen sulphide - H₂S (sour corrosion), fluid temperature, water salinity, water cut, fluid dynamics, and pH [5-7].

The damage of carbon steel alloy base due to the exposal of corrosive fluid components has piqued interests from researchers, mainly because of the existence of CO₂ and other impurities that are commonly present in oil and gas fluids, which cause not only general corrosion but also localised corrosion. Adjacent to that, CO₂ components and other impurities existence are potential to the decrease of material's thickness which leads to weight loss, pitting, and sulphide/chloride stress cracking. It eventually depends on how much CO₂ and other impurities existence and the possibility of other water phase and hydrocarbon occurrence.

With environmental conditions that contain high levels of CO₂, H₂S and chloride, it is necessary to select the right material for these environmental conditions. The following are some possible materials to replace conventional carbon steel in these harsh environments:

1. Stainless steels
Ferritic, martensitic and austenitic stainless steel materials are available in the form of iron-chromium alloys. Additional alloying element such as

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molybdenum, nickel or carbon may be added to form certain microstructure and improve specific properties including strength, corrosion and high temperature resistance. [8].

2. Duplex stainless steels
 DSS is a Austenitic-Ferritic stainless steel which was developed to combat corrosion problem caused by chloride-bearing cooling waters and other aggressive chemical process fluids. This material contains 21-23% chromium, 4.5-6% nickel, and 2.5-3.5% molybdenum [8].
3. Super duplex stainless steels
 SDSS refers to high performance DSS with a improved pitting and crevice corrosion resistance. This material contains 24-26% chromium, 6-8% nickel, and 3-4% molybdenum. With high chromium content this material has excellent resistance to acid chlorides, acids, caustic solutions, and other harsh environment [8].
4. Alloy 825
 Alloy 825 is a nickel-iron-chromium alloy with addition of molybdenum, copper and titanium. This material contain 19.5-23.5% chromium, 38-46% nickel, and 2.5-3.5% molybdenum. High nickel content in this material gives the allot virtual immunity to stress corrosion cracking (SCC) and good resistance to pitting and crevice corrosion [8].
5. Alloy 625
 Alloy 625 is an outstanding resistant material to pitting and crevice corrosion. This material contains 20-30% chromium, a minimum 58% nickel and 8-10% molybdenum. This alloy also has extremely high resistance to attack by a wide range of media environment including sulphuric, phosphoric, nitric, and hydrochloric acid as well as alkalis and organic acids in both of reducing and oxidising conditions[8].

This paper discusses the process of selecting initial materials in a program plan based on existing conditions, which the material used is duplex stainless steel with a content of 15Cr and 22 Cr.

2 Methodology

This study based on provided data which have actual condition of relatively high on oil and gas field:

- CO₂ 25 %mol,
- H₂S 1-1.2 %mol
- Chloride ions up to 10.000 ppm
- Temperature up to 80°C

2 (two) material types will be selected as early prediction material, which are material with 15% chrome and 22% chrome that are widely known for corrosion resistance alloys (CRA).

Both of samples are commercial grade materials and the composition is tested by Optical Emission Spectroscopy to calculate the Pitting Resistance

Equivalent Number (PREN). The potentio-dynamic test was performed in the chloride solution with temperature as the parameter. The temperature was set into three area, ambient (27°C), medium (50°C) and high temperature (80°C).

3 Results And Analysis

3.1 Composition of Materials Test

Materials composition test using spectrometer on two CRA materials (15Cr and 22Cr) shows each mixed compositions as follows on Table 1. The result showed that duplex 22Cr has higher amount of Molybdenum and Vanadium in their composition. Both of the element is already known for their ability to improve the pitting resistance of CRA materials.

Table 1. Composition of Materials Sample Test SS 15Cr and 22Cr (element in %)

Sample	Fe	Cr	Mo	Ni	V
15Cr	75.6	15.1	2.02	5.44	0.043
22Cr	66.3	23.0	3.34	4.69	0.072

Pitting resistance equivalent number (PREN) is a prediction for pitting corrosion resistance of stainless steel material and calculated based on the chemical composition. the higher PREN-value, has more pitting resistant compare to the lower materials. The pitting resistance equivalent number was calculated using the equation below:

$$\text{PREN} = \text{wt.\%Cr} + 3.3 \text{ wt.\%Mo} + 20 \text{ wt.\%N} \quad (1)$$

For the sample uses in this experiment, calculated PREN for 15Cr is 21.8 and 36.9 for sample test 22Cr.

15Cr steel is a martensitic stainless steel which is applicable in CO₂ and CO₂ + slight H₂S environment at temperature up to 200°C. This material is superior to conventional duplex stainless steel and nickel based alloy in terms of available size range, delivery and cost [9]. Whereas, 22Cr is a duplex steel grade with ferritic-austenitic microstructure. This alloy has outstanding corrosion resistance to seawater, most concentration of sulphuric acid and sulphide stress corrosion cracking (sour-gas environment) [10].

3.2 Polarization Test

Polarization test using cyclic method on 2 CRA materials (15Cr and 22Cr) shows the result comparison of potential value differences in varied condition as showed in table 2. The result showed the pitting tendency in the materials. High Epit-Ecorr showed the possibility of deep pit formation. While the other condition showed the shallow pit formation. Duplex relatively have high value

which indication the corrosion morphology is local while the 15Cr will shallower than duplex. The other interesting result is showed in carbon steel corrosion rate. CO₂ corrosion is the fastest corrosion rate, and presence of H₂S reduce the corrosion rate.

Table 2. CRA Corrosion Potential and Corrosion Rate base on the Calculations of the Carbon Steel

TEMPERATURE		ROOM (27°C)			MEDIUM (50°C)			HIGH (80°C)		
Cr (ppm)	Condition	E _{pit} - E _{corr} (mV)		mpy	E _{pit} - E _{corr} (mV)		mpy	E _{pit} - E _{corr} (mV)		mpy
		15-Cr	Duplex		CS	15-Cr		Duplex	CS	
5,000	Natural	768	1325	0.01	600	1400	0.002	700	1000	0.06
	CO ₂	996	1455	40.24	575	1365	86.32	480	656	88.8
	H ₂ S	650	1230	24.86	600	1110	31.56	250	520	62.6
	CO ₂ + H ₂ S	700	1335	29.43	600	1157	29.5	550	680	51.64
18,000	Natural	618	1374	0.01	650	1025	0.02	425	575	0.07
	CO ₂	598	1350	45.32	525	975	97.12	550	475	100.1
	H ₂ S	624	990	27.99	475	1150	35.54	350	400	70.5
	CO ₂ + H ₂ S	644	910	32.71	425	1200	33.23	450	550	58.16
25,000	Natural	604	1432	0.01	275	1000	0.02	325	350	0.07
	CO ₂	858	1482	48.05	400	1250	102.98	350	500	106.04
	H ₂ S	802	1300	29.68	325	1150	37.68	150	400	74.76
	CO ₂ + H ₂ S	375	1225	34.69	375	775	35.23	350	425	61.67

3.3 Interpretation of test polarization 5,000 ppm Cl⁻ 1 atm CO₂ with room temperature at 27 °C

In polarization curve (Figure 1) the tendency of pitting occurrence is displayed on material sample test of 15% Cr and Duplex, which is illustrated as looping line or hystericist. On material sample test 15% Cr will experience higher chance of pitting compared to duplex material sample test, that is shown by the relatively small area of duplex. On material sample test of 15% Cr component, critical pitting potential occur on potential value of +0.700 V SCE and its protection potential approximately +0.300 V SCE.

On the other hand, the critical pitting potential of Duplex occur on +1.400 V SCE and its protection potential is +1.200 V SCE, in which this condition will not develop the well activation and the existing hole will remain passive.

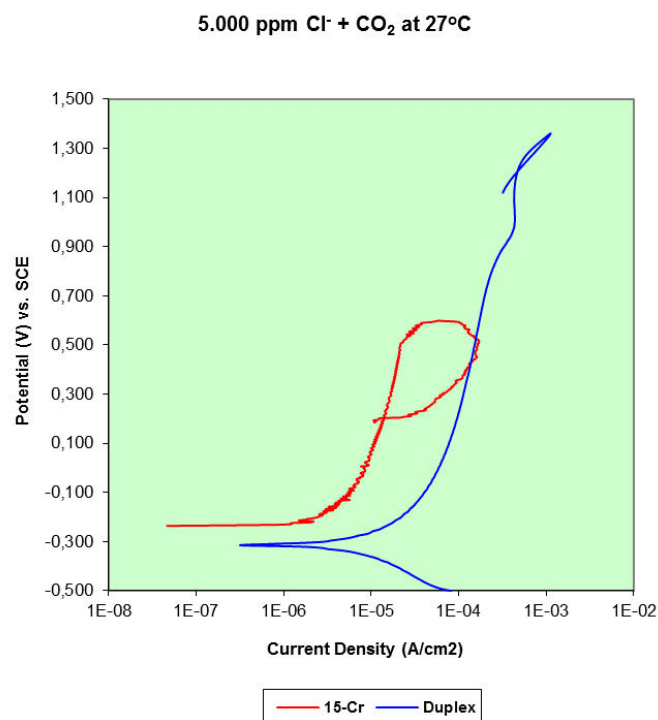


Fig. 1. Polarization Curve at 5,000 ppm Cl⁻, 1 atm CO₂ at Room temperature (27 °C).

4 Conclusion

1. The result of chrome 15 %Cr material polarization test has the tendency of pitting occurrence, which has happened on chloride ion 5,000 ppm in room temperature 27 °C.
2. The result of chrome 22 %Cr material polarization test in room temperature (27 °C) and medium (50 °C), the pitting tendency occur in chloride ion 25,000 ppm, while the pitting in high temperature (80 °C) in chloride ion 5,000 ppm has occurred.

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