Performance of Nickel-Coated Manganese Steel in High-Chloride Low-Sulphate Seawater Environments

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ABSTRACT

This work investigated the service performance of nickel-coated manganese steel in both normal high-chloride (clean) and low-sulphate high-chloride (polluted) seawater environments (typical offshore oil and gas production environments). Structural manganese steels coated with nickel together with the control were tested for corrosion characteristics using the weight loss method. It was found that the nickel coat was able to resist corrosion overtime via spontaneous formation of passive oxide films at ambient temperatures. Analysis of resulting corrosion rates underscored the viability of nickel coating at inhibiting severe corrosion owing to the harsh chloride- and sulphate-containing seawater typical of the oil and gas production environments.

Keywords: passive oxide, corrosion, high-chloride low-sulphate seawater, manganese steel, electroplating,

1. INTRODUCTION

It is estimated that industry spends $276 billion annually on corrosion. These costs arise from a variety of areas. Prevention, monitoring, and repair are the main contributors to this high amount and these values do not even include down time as a result of corrosion [1, 6].

Corrosion is the deterioration of a material or its properties in a given service environment. It is also the partial or complete wearing away, dissolving, or softening of any substance by chemical or electrochemical reaction with its environment. The term *corrosion* specifically applies to the gradual action of natural agents, such as air or salt water, on metals. It is a state of deterioration in metals caused by oxidation or chemical action [10]. The basic corrosion cell is formed by two dissimilar metals immersed in an electrolyte joined by a conductor, One electrode will tend to corrode more readily than the other and is called the anode. Natural systems often place the machine part as the anode while the prevailing environment makes up the electrolyte [8, 9].

The oil industry consists of the upstream businesses of exploration & production and gas & power and the downstream businesses of oil products, chemicals and oil sands. Corrosion attacks every component at every stage in the life of every oil and gas field. At the drilling stage (which is about the first stage in production), oxygen-contaminated fluids are first introduced. Water and carbon-dioxide—produced or injected for secondary recovery—can cause severe corrosion of completion strings. Hydrogen sulphate in the plant effluents poses severe environmental hazards. This makes the surrounding water and atmosphere hostile to metallic tools and parts [4, 7].

Several established and emerging technologies for corrosion evaluation and monitoring abound. Established technologies include measuring environmental conditions, exposing material coupons to corrosive media, and using electrical resistance, linear polarization resistance, and galvanic probes. Emerging technologies include the use of advanced electrochemical testing techniques and the application of specialized probes for stress-corrosion cracking and pitting corrosion [4, 5, 9]. Since it is almost impossible to prevent corrosion, it is becoming more apparent that *monitoring* and *controlling* the corrosion rate may be the only economical solution. The oil industry has invested heavily in material and personnel to try to tame corrosion and prevent ferrous tools from returning to their natural state. New oil fields benefit from predevelopment planning and the growing knowledge of all aspects of corrosion control and monitoring [2. 3]. A large volume of research work has been done to proffer solution to corrosion phenomenon. The present work understudies the performance of nickel-coated manganese steel in two environments which represent the oil and gas production environments of normal high-chloride (clean) and low-sulphate high-chloride (polluted) seawater.

2. MATERIALS AND METHOD

2.1 Description of Steel Samples

The steel material used for this experiment is ST60Mn steel obtained from the standard stock with the chemical composition (wt%) of carbon 0.35-0.42, silicon 0.20-0.30, manganese 0.90-1.20, phosphorus 0.04, sulphur 0.25, copper 0.10, chromium 0.10, nickel 0.10; the balance being iron. From this steel, 30 pieces of about 10 mm square samples were prepared.

2.2 Corrosion Media

Two corrosive environments were prepared:
(i)   High chloride seawater environment from the Atlantic Ocean.
(ii)   Simulated low-sulphate high-chloride environment obtained by adding 0.015M Na_2SO_4 to seawater sourced from the Atlantic Ocean.

In general, these two environments represent the oil and gas production environment of normal high-chloride (clean) and low-sulphate high-chloride (polluted) seawater environments.

2.3 Electroplating

To obtain good adhesion and brightness of the nickel coat on the substrates, the nickel solution for a 3 litres plating bath was prepared using 600 g of nickel sulphate, 120 g of nickel chloride, 120 g of boric acid, 60 ml of formaldehyde and 3 litres of distilled water. Using a nickel anode, the steel samples were electroplated for 40 and 50 minutes respectively. The electrolyte having being preheated to 50°C. After electrolysis the specimens were removed, rinsed in distilled water and left to cool off in sawdust. Only 20 samples were electroplated while the remaining 10 were left as control. After electroplating, the initial weights of all samples were measured and recorded using a digital weighing balance.

2.4 Corrosion Test

A group of three samples (comprising an uncoated sample and two samples each coated for 40 and 50 minutes respectively) was suspended from strings and completely immersed in high-chloride seawater contained in clean HDPE bowls for 6 days. After this period of complete immersion, the samples were removed, cleaned and weighed (final weight). This was repeated for another four groups but with immersion durations of 12, 18, 24 and 30 days respectively. In the same vein, five groups of samples were suspended from strings and completely immersed in high-chloride low-sulphate seawater for 6, 12, 18, 24 and 30 days respectively. The final weights were measured and recorded.

2.5 Corrosion Rate Measurement

Corrosion rate measurement was obtained from the weight loss method using the standard corrosion rate formula.

$$C.R. = \frac{kW}{DAT}$$

Where,
W= weight loss (g); D = density (g/cm^3); A = Area (cm^2); T = Time (hrs)
K = corrosion constant which will depend on the dimension desired for the corrosion rate (8.76 x 10^4 for mm/year).

3. RESULTS AND DISCUSSION

3.1 Trend of Corrosion Rate

Corrosion rates for curves of Figure 1 decrease non-uniformly with time for any given sample. Each corrosion rate curve is characterized with an initial peak owing to rapid interaction between the samples and their environment. Curves of Figure 2 also manifest similar initial peaks. Beyond six days, the rates of corrosion fall significantly. This rapid decline is due to prompt formation of passivating oxide films on the surface of immersed samples. It was observed that

the electrodeposited nickel coat on the steel gave it a protection against corrosion. The passivating film which builds up on the surfaces of the samples are actually corrosion products which serve to inhibit further corrosion.
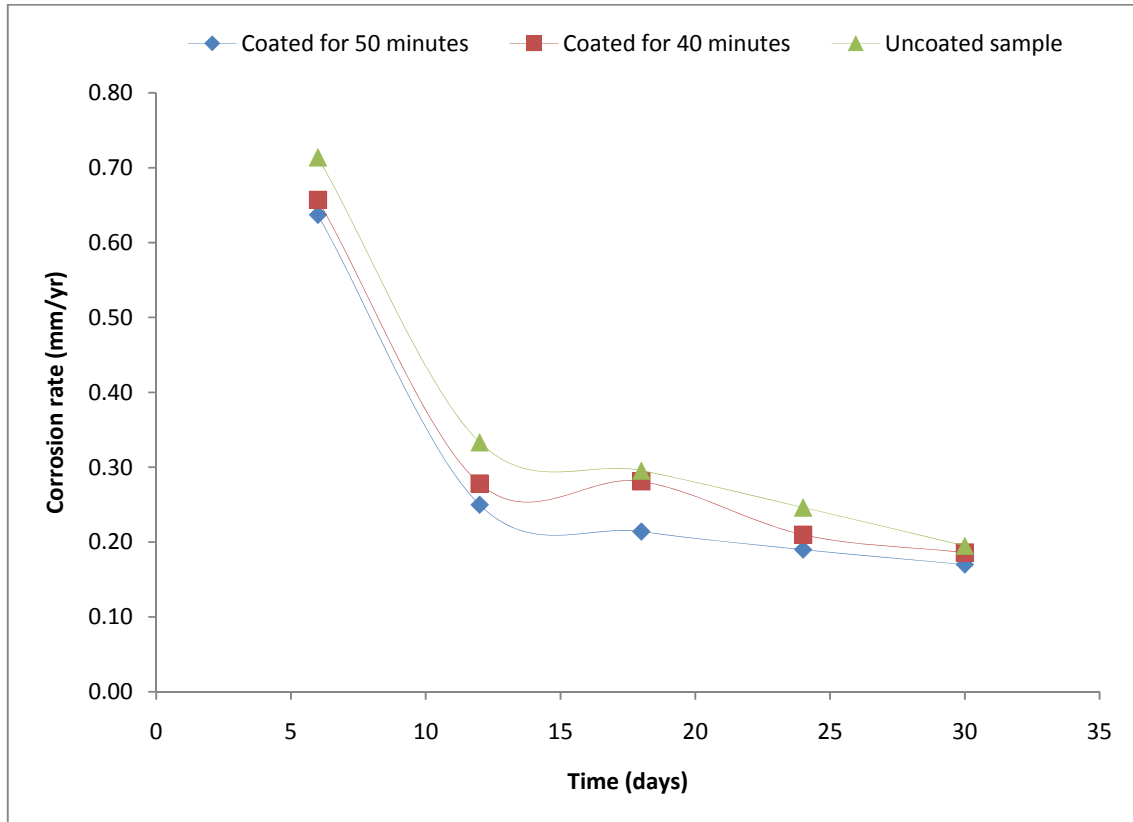

Figure 1: Corrosion rates of samples immersed in high-chloride seawater as a function of time

Beginning from 14 days down to 30 days the curves of corrosion rates of all the samples attempt to stabilize to a linear horizontal trend with a gentle slope. The curves of Figure 2 show a steeper slope than those of Figure 1 suggesting higher corrosion rates in the samples subjected to high-chloride low-sulphate environment. This observation again bring to the fore the more severe corrosion tendency of dissolved sulphur polluted seawater.

3.2 Corrosion Rates in High-Chloride Environment versus High Chloride Low-Sulphate Environment

The initial corrosion rates (at six days) is higher for all the samples in high-chloride low-sulphate seawater environment than in high chloride seawater environment. Although the active corrosion products in seawater are the dissolved salts of which sodium chloride is chief, the presence of sulphur readily exacerbates corrosion as is demonstrated in this work. On the average, judging from Tables 1 and 2, the corrosion rate is increased by 5—25 % by the presence of dissolved sulphur even at a low concentration for uncoated samples while the nickel coating reduced this corrosion rate to a maximum of 7—10 %.
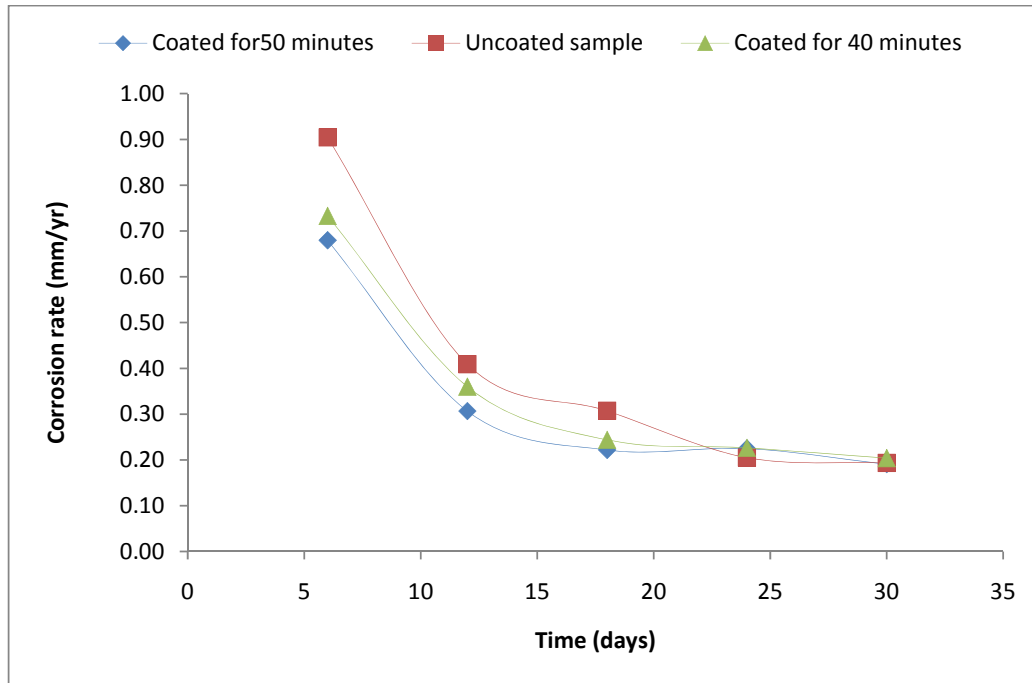
Figure 2: Corrosion rates of samples immersed in high-chloride low-sulphate seawater as a function of time

Table 1: Corrosion rates of samples immersed in high-chloride seawater

	Sample	Area (cm^2)	Initial weight (	Final weight (	Weight loss (g)	Days	Time (hrs)
UNCOATED SAMPLE	F	7.21	11.157	11.091	0.066	6	144
	G	6.67	9.260	9.203	0.057	12	288
	H	7.92	12.562	12.472	0.090	18	432
	I	6.97	10.971	10.883	0.088	24	576
	J	7.36	11.459	11.367	0.092	30	720
COATED FOR MINUTES	F1	6.41	9.053	8.999	0.054	6	144
	G1	6.59	9.072	9.025	0.047	12	288
	H1	7.12	10.463	10.386	0.077	18	432
	I1	6.32	8.350	8.282	0.068	24	576
	J1	6.54	8.370	8.292	0.078	30	720
COATED FOR MINUTES	F2	6.12	8.017	7.967	0.050	6	144
	G2	7.65	8.088	8.039	0.049	12	288
	H2	6.44	8.309	8.256	0.053	18	432
	I2	7.29	8.574	8.503	0.071	24	576
	J2	8.17	12.718	12.629	0.089	30	720

Table 2: Corrosion rates of samples immersed in high-chloride low-sulphide seawater

Sample		Area (cm²)	Initial weight (g)	Final weight (g)	Weight loss (g)	Days	Time (hrs)	Corrosion rate (mm/yr)
UNCOATED SAMPLES	A	5.95	11.486	11.417	0.069	6	144	0.9044
	B	7.91	12.623	12.540	0.083	12	288	0.4092
	C	7.70	12.001	11.910	0.091	18	432	0.3072
	D	7.60	9.272	9.192	0.080	24	576	0.2052
	E	5.96	7.500	7.426	0.074	30	720	0.1937
COATED FOR 40 MINUTES	A1	7.66	11.802	11.730	0.072	6	144	0.7331
	B1	7.69	12.365	12.294	0.071	12	288	0.3600
	C1	6.18	8.218	8.160	0.058	18	432	0.2440
	D1	6.89	9.902	9.822	0.080	24	576	0.2264
	E1	7.19	10.482	10.388	0.094	30	720	0.2039
COATED FOR 50 MINUTES	A2	6.77	9.218	9.166	0.052	6	144	0.5990
	B2	5.85	7.676	7.630	0.046	12	288	0.3066
	C2	6.45	8.707	8.652	0.055	18	432	0.2217
	D2	6.42	8.815	8.741	0.074	24	576	0.2247
	E2	5.97	7.989	7.916	0.073	30	720	0.1907

Many aqueous corrosion problems may be handled by using nickel and its alloys. The nickel coat has a good resistance to corrosion at ambient temperatures to high chloride and low sulphate seawater environments. Nickel spontaneously forms passive oxide films upon exposure to seawater at ambient temperature. This film helps to provide useful corrosion resistance which subsequently reduces corrosion rate overtime.

4. CONCLUSION

The following conclusions can be drawn from the experiment described above.
1. High-chloride low-sulphate seawater (polluted) environments are more corrosive than high-chloride (clean) seawater environments.
2. Sulphate pollution in seawater increases corrosion rate of manganese steels by 5—25 % for uncoated samples and this is reduced to 7—10 % by electrodeposited nickel coating.
3. A thicker coat of electrodeposited nickel provides better corrosion resistance through formation of passivating oxide layers at the surface of the steels.

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