Effect of salinity on the corrosive wear behaviour of engineering steels in aqueous solutions

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ABSTRACT

The effect of salinity is assessed on the corrosive wear behaviour of a low-alloy steel (UNS G43400) and three stainless steels (UNS S15500, UNS S31600 and UNS S32760). Erosion-corrosion testing was conducted using a submerged impingement slurry jet test-rig. Three salinities were evaluated; 0.05%NaCl, 3.5%NaCl and 10%NaCl. Total volume losses (TVL) and a volumetric analysis technique were used to assess the damage in the directly-impinged zone (DIZ) and outer area (OA). Under all measured parameters, material loss for the stainless steels increased marginally with increased salinity. In terms of TVL and OA volume loss, the low alloy steel exhibited significantly greater material loss from 0.05%NaCl to 3.5%NaCl conditions, however, no further increase was evident when the salinity was raised to 10%NaCl.

Keywords

Corrosion-wear, steel, slurry erosion, surface analysis

1. INTRODUCTION

Corrosive wear is a damage mechanism that affects materials in contact with an aqueous solution and is the combined effect of corrosion and wear by the agitation of surrounding fluids, especially if they contain abrasive/erosive particles. This causes accelerated component failure and is prevalent in industries such as oil and gas production and mining, affecting fluid transport components. Due to the significant problem that it poses, a large amount of work has been conducted in recent years by researchers to understand how corrosive wear is affected by a multitude of different factors [1]. These factors have been consolidated into three groups by Poulson [2], and Neville et al. [3], namely:

- material composition and properties such as hardness, toughness, etc. [4];
- hydrodynamic conditions such as the velocity and angle of attack of the solution across the material surface [5, 6], and the flow regime [7];
- environmental properties such as solution temperature and pH [8, 9], and sand loading [7].

Another important factor that must be considered is the influence of salinity (total dissolved solids, TDS) of the aqueous fluid and its effects on material degradation.

Water salinity will vary from different sources, regionally as well as internationally [10]. This means that the same type of fluid-transport equipment may be deployed in locations with widely differing water salinities. For example, seawater in the Persian Gulf can contain more than 5%TDS, compared to the world average of about 3.5%TDS, and desalination processes can have fluids of widely different salt contents throughout the system [11]. Additionally, industry is increasingly looking to recycle water used in processes to combat scarcity restrictions and sustainability demands [12–17]. Often such recycled water, e.g. flowback water in oil/gas extraction and wastewater from mining operations, tends to be more saline than when first utilised [18–22]. In light of this, it is clear that understanding the effect of salinity on the corrosive wear performance of engineering materials is worth investigating in detail.

Previous studies [23–26] have given some attention to the influence of salinity on the corrosion behaviour of carbon- and low-alloy steels in differing aqueous solution chemistries (such as neutral, alkaline and CO₂/H₂S-containing solutions). However, few experimental investigations have been conducted to assess the effect of salinity in corrosive wear conditions. Earlier investigations assessing corrosive wear have largely been carried out to compare the corrosive wear performance of materials, including stainless steels, in a single solution salinity [4, 27]. Often, the corrosive wear results are separated into the three main damage mechanisms of erosion, corrosion and synergy (erosion-enhanced corrosion and corrosion-enhanced erosion). The scope of such studies should be enhanced by expanding the range of salinities in which materials are tested.

An early comprehensive study by Uhlig and Morrill [28] explored the effect of sodium chloride concentration on the pure corrosion of 18Cr-8Ni stainless steel and mild steel in slightly turbulent conditions. Tests were conducted at 90°C for 24 hours in a salinity range of 0-25%NaCl. The study showed that the mass loss of both materials increased as the salinity of the solution increased from distilled water; both materials had a maximum mass loss at a certain salinity (4%NaCl for the 18Cr-8Ni stainless steel and 2%NaCl for the mild steel), and the mass losses decreased past the maximum towards 25%NaCl. With both steel grades, therefore, the maximum damage through corrosion occurred around the average salinity of seawater (3.5%NaCl) and the relationship was particularly sensitive in that salinity region.

Zhao et al. [29] reported, in their study on the corrosive wear behaviour and corrosion resistance of AISI 316 stainless steel, that the damage measured on samples in jet impingement experiments using “sea sand” was greater than with silica sand. The water used for experiments was tap-water, so NaCl salt crystals present in the “sea sand” (0.21wt%Cl⁻) dissolved and marginally raised the salinity of the aqueous solution. As a result, corrosion of the stainless steel was accelerated throughout the duration of “sea sand”

experiments and the mass losses were correspondingly higher than with silica sand (roughly 20% higher after 6 hours and 43% higher after 12 hours, at 60° impact angle).

Studies, which directly investigate the effect of salinity on the corrosive wear of materials in a controlled manner, have tended to make use of only two salinities, namely 3.5%NaCl (mimicking seawater) and freshwater (nominally 0.05%NaCl). One such study was conducted by Neville and Hodgkiess [30] and assessed the corrosive wear of an austenitic stainless steel (UNS S31603). The mass loss of the stainless steel was 7.4% greater in the higher salinity solution after 1-hour impingement. A breakdown of the erosive, corrosive and synergistic mass losses showed that, in the seawater solution, the corrosion component had grown from 0.4% to 2% of the total mass loss, while the synergy (corrosion enhanced erosion) had grown from 0.6% to 16.8%. Combining the corrosion and synergy components revealed that the mass loss influenced by corrosion in the higher salinity solution constituted 18.8% of the total mass loss, up from 1% in freshwater. Therefore, not only did the salinity affect the electrochemical (corrosive) damage but also the mechanical damage by amplifying the synergy component. Another study by Neville et al. [31] performed similar analysis on a grey cast iron (BS 1452) and found that, at various levels of sand loading in solid-liquid impingement erosion-corrosion conditions, the material degradation of the cast iron was lower in the lower salinity conditions compared to 3.5%NaCl by nearly 50%.

Chen et al. [32] examining the tribocorrosion behaviour of Inconel 625 sliding against 316 stainless steel, found that the wear on both materials was greater in 3.5%NaCl solution compared to distilled water at two sliding forces (100N and 400N). Another finding was that the maximum corrosion rate of the Inconel 625 alloy occurred in 3%NaCl solution after conducting potentiodynamic polarisation scans on the alloy in a range of solutions from 0.5%NaCl to 4%NaCl. This maximum corrosion rate and subsequent corrosion rate decrease beyond 3%NaCl was attributed to the synergism of salinity and oxygen concentration. Chen et al. [32] also stated that, because the higher conductivity of more saline water increases the corrosion rate, and in corrosive wear scenarios passive films are quickly removed, increased solution salinity accelerates wear loss in tribocorrosion.

There has also been some investigation of salinity effects under cavitation conditions. Gou et al. [33] tested ASTM 1045 carbon steel in a broad range of salinities to explore the effect of silica sand on this phenomenon. Vibratory cavitation tests were carried out on the steel for 260 minutes in seven different solution concentrations ("tap water", 0.5%NaCl, 1%NaCl, 1.5%NaCl, 3.5%NaCl, 10%NaCl and 15%NaCl) before assessing the damage by measuring the ensuing mass loss. As the salinity increased, damage by cavitation, abrasion and corrosion increased sharply before stabilising around 3.5%NaCl, beyond which the mass loss increased at a significantly reduced rate. It was postulated by the authors that the increased

salinity restricts the average diameter of cavitation bubbles, thus limiting the mass loss above seawater conditions.

A further study by Wu et al. [34] examined the effect of salinity on corrosive wear, focused on cavitation erosion in particular, and found no difference in mass loss, surface roughness and hardness after 300-minute duration cavitation erosion testing of five alloys (SUS304 stainless steel, a Ni-based self-fluxing alloy – Ni-17wt.%Cr-3.3wt.%B-4.3wt.%Si-4.2wt.%Fe-0.9wt.%C, Ti₄₉Ni₅₁, Ti₅₀Ni₅₀ and Ti₅₀Ni₄₀Cu₁₀) in freshwater and 3.5%NaCl solutions. This was due to the excellent corrosion resistances of the tested alloys [34]. However, in a study investigating the corrosive wear of pure iron and selected cast irons in cavitation conditions, Tomlinson and Talks [35] were able to show that, for these metals, salinity does affect the cavitation rate. Grey cast irons are particularly susceptible to severe cavitation erosion damage because of weak graphite flakes present throughout large volumes of the metal matrix. The materials were tested in distilled water, 0.02%NaCl solution and 3%NaCl solution and, in almost every case, the cavitation rate increased with rising salinity. The cavitation-erosion rate of pure iron increased by a factor of 1.4 as the salinity was raised from distilled water to 3%NaCl. Most of the cast iron grades tested exhibited an increase in erosion rate of 4 or 5 times, while one grade (carbide network in pearlite with a 25µm nitrided layer) had a cavitation rate 19.6 times greater in the higher salinity conditions.

In summary, there has been almost universal evidence from previous work of enhanced corrosive and corrosive wear degradation of materials at moderate levels of salinity. At salt concentrations exceeding 3.5%, however, investigations have been rare and the findings are less consistent with some evidence of different material loss/salinity relationships between different engineering steels.

This study seeks to extend the scope of work which evaluates the effect of salinity on the corrosive wear of engineering steels. One feature of the investigation was to probe the response of different classes of steels to a range of salt concentrations. In addition to assessing the behaviour of a high-strength, low-alloy steel, the work included the comparative examination of the influence of steel microstructure (martensitic, austenitic and duplex) in three grades of stainless steels. A jet impingement apparatus was used to direct a two-phase flow of water and silica sand onto the test subjects. The effect of salinity on the corrosive wear damage of the alloys was evaluated using a comprehensive experimental/analytical procedure. This involved measuring the total volume losses sustained followed by topographical analysis of tested specimens [36] that allowed the material loss to be distinguished between two hydrodynamic regions on the specimen surface. Additional understanding of the deterioration mechanisms was obtained from undertaking post-test microstructural examination of specimens.

2. MATERIALS AND METHODS

The four alloys considered in this study comprised a medium carbon low-alloy steel (UNS G43400), a precipitation hardened martensitic stainless steel (UNS S15500), an austenitic stainless steel (UNS S31600) and a superduplex stainless steel (UNS S32760). Microstructural images of the four test materials are illustrated in Figure 1. 2% Nital was used to reveal the microstructure of UNS G43400, whereas, the stainless steel alloys were electrolytically (1V DC) etched with 10% oxalic acid. Thus, any effect of stainless steel microstructure was also assessed. The nominal chemical composition of each steel is presented in Table 1, and the measured hardness and nominal density of each steel are displayed in Table 2.

Figure 1: *Microstructure images of A - tempered martensite of UNS G43400; B – tempered martensite with retained austenite of UNS S15500; C – ferrite/austenite duplex structure of UNS S32760; D – austenite with delta ferrite stringers in UNS S31600*

Mass loss tests were carried out in free erosion-corrosion (FEC) solid-liquid impingement conditions with a recirculating submerged impingement slurry jet test-rig [37]. The duration of the tests was 1 hour. Slurry impinged at an angle of 90° upon the specimen surface through a nozzle of 4mm diameter at 18m/s with a temperature of 40±2°C. The nozzle was offset from the specimen surface by 5mm. Three slurries were employed to observe the effect of salinity and they consisted of 500µm spherical silica sand particles suspended in 0.05%NaCl, 3.5%NaCl and 10%NaCl aqueous solution. The sand concentration was measured to be 0.5g/l. The specimens (38mm diameter and 17mm thick) were ground to 1200 grit paper prior to

testing. A mass balance with an accuracy of $\pm 0.1\text{mg}$ was used to measure the mass loss of the test samples. After FEC tests, the UNS G43400 samples were briefly immersed in an inhibited acidic solution (Clark's solution) to remove corrosion product from the test surface. The measured mass losses were converted to volume losses using the nominal density of the respective steel. Macro-hardness measurements of the test materials were taken with a calibrated Vickers hardness testing apparatus with a 5kgf load.

Impressed current cathodic protection (ICCP) tests were also performed to isolate the pure mechanical damage. The electrode potential for the CP tests was set at -0.8V (Ag/AgCl) – this being the generally-adopted target, used in industry, for carbon steels and low-alloy steels. For consistency, the same potential was adopted for the three stainless steels after establishing that back-extrapolation of anodic polarisation plots indicated (for example: Figure 2) residual anodic rates at -0.8V , below 0.0005 mA/cm^2 which represents negligible rates of metal loss.

Figure 2: Typical anodic polarisation plots with back extrapolation demonstrating negligible corrosion rates at an applied electrode potential of -0.8V (Ag/AgCl)

Post-test surface analysis of FEC specimens was facilitated using SEM (Hitachi SU-6600) with a 15kV accelerating voltage. The wear scar topography (depth and volume) of the tested materials (FEC and ICCP) was assessed using an Alicona InfiniteFocus 3D optical profilometer with a wear scar volume accuracy of $\pm 0.02\text{mm}^3$. Such surface profiling facilitates the separation of material losses between the directly-impinged zone and the outer regions of the specimens. In combination with the results from the application of cathodic protection, the influence of salinity on pure mechanical and corrosion-related phenomena was assessed. The corrosion-related damage figures quoted herein of course include the sum of pure corrosion plus the synergy (composed of 'Erosion-enhanced corrosive attack' and 'Corrosion-

enhanced erosion damage'). The focus of this paper, however, has been to report the major overall findings in terms of how salinity affects the total corrosive wear damage, as well as in two different hydrodynamic zones together with an assessment of the role of cathodic protection in eliminating the corrosion (including synergy) role. The sub-division of the corrosion-related damage into its separate components (including synergy) will be considered in a later paper [38].

Table 1: Nominal chemical composition (%wt) of the tested steels.

Material	C	Cr	Ni	Mn	Si	Mo	S	N	P	Cu	W	Fe
UNS G43400	0.37-0.43	0.7-0.9	1.6-5.2	0.6-0.8	0.15-0.3	0.2-0.3	0.04	-	0.035	-	-	Bal.
UNS S15500	0.07 max.	14-15.5	3.5-5.5	1max.	1max.	-	0.03 max.	-	0.04	2.5-4.5	-	Bal.
UNS S31600	0.08 max.	16-18	10-14	2max.	0.75 max.	2-3	0.03 max.	0.1 max.	0.045 max.	-	-	Bal.
UNS S32760	0.03 max.	24-26	6-8	1max.	1max.	3-4	0.01 max.	0.2-0.3	0.03 max.	0.5-1	0.03 max.	Bal.

Table 2: Measured hardness with standard deviation and nominal density of the tested materials.

Material	Hardness (HV – 5kgf)	Density (g/cm ³)
UNS G43400	300 ± 9	7.85
UNS S15500	360 ± 11	7.80
UNS S31600	170 ± 5	8.00
UNS S32760	265 ± 7	7.80

3. RESULTS

3.1 Volume loss measurements

Figure 3 displays the total average volume loss (TVL) results for each of the four test materials after solid-liquid erosion-corrosion testing in all three salinities, and with the application of ICCP. The error bands represent the experimental scatter of results from at least three test replicates. The low-alloy steel (UNS G43400) was observed to experience much greater corrosive wear damage across the range of salt concentrations compared to the stainless steels, particularly at the higher salinities. The experimental scatter exhibited by the low-alloy steel can be attributed to material loss which has been predominately caused by corrosion-related damage associated with non-uniform distribution of non-metallic inclusions. Of all the tested materials, the superduplex stainless steel (UNS S32760) performed the best, with the lowest TVL in every test condition.

As shown in Table 3, all three stainless steel alloys exhibited continual increases in TVL as the salinity increased with evidence that the incremental change in material loss was maintained up to 10%NaCl. This was especially evident for the UNS S31600 and UNS S15500 alloys. In contrast, the TVL of the low-alloy

steel increased sharply from 0.05%NaCl to 3.5%NaCl (Figure 3). As the concentration was raised to 10%NaCl, however, there was no obvious increase in erosion-corrosion damage.

When ICCP was applied to evaluate the pure mechanical damage, the volume loss of the UNS G43400 dropped dramatically (21%, 70% and 65% reductions compared to 0.05%NaCl, 3.5%NaCl and 10%NaCl FEC volume losses respectively), highlighting the large proportion of corrosive wear damage in low-alloy steels which is associated with corrosion-related deterioration. ICCP also had some effect in reducing the material loss of the stainless steel alloys, particularly in the high saline solution of 10%NaCl (26-29% reductions in material loss). These results show that there is an increase in corrosion-related damage for stainless steels as the salt content is increased, though to a far smaller degree than with the low alloy steel. This reduction in TVL provided by ICCP has been demonstrated in previous studies in 3.5%NaCl which assessed a wide range of materials such as a carbon steel, austenitic, martensitic, superaustenitic and duplex stainless steels [4, 27, 39, 40].

Figure 3: Total volume loss of all tested materials in each salinity and ICCP

Table 3: Percentage differences in TVL for the tested steel alloys with increasing salinity

Test material	Percentage difference 0.05%NaCl → 3.5%NaCl	Percentage difference 3.5%NaCl → 10%NaCl
UNS S31600	8% increase	20% increase
UNS S15500	8% increase	20% increase
UNS S32760	16% increase	10% increase
UNS G43400	162% increase	14% decrease

3.2 Post-test surface topography and analysis

Three-dimensional surface topography was conducted on each of the FEC and ICCP test specimens to quantify the material loss in the wear scar – directly under the impinging jet - an example of which is shown in Figure 4.

Figure 4: 3D surface topography scan on the wear scar of the UNS S15500 stainless steel surface after solid-liquid impingement

Volume losses in the directly impinged zone (DIZ), as ascertained through the 3D surface topography scans for all tested materials in each test condition, are displayed in Figure 5. These volume losses universally increase (by different proportions as shown in Table 4) with salinity, strongly suggesting a link between salinity and the erosion-corrosion process within the DIZ. The superduplex stainless steel (UNS S32760) had the lowest DIZ volume loss of all the tested materials and the low-alloy steel (UNS G43400) had the highest, mirroring the observed TVL behaviour shown in Figure 3. Both lower-grade stainless steels, UNS S31600 and UNS S15500, exhibited greater volume loss compared to UNS S32760 in the high saline 10%NaCl solution. Similar trends to TVL were observed in terms of material loss increase for the stainless steels with increasing salinity. Both UNS S31600 and UNS S15500 demonstrated lower percentage increases in material loss from 0.05%NaCl to 3.5%NaCl compared to UNS S32760. However, when salinity was increased from 3.5%NaCl to 10%NaCl, both UNS S31600 and UNS S15500 experienced significantly greater percentage increase in material loss compared to UNS S32760. This trend was similar to that observed in Table 3 for TVL.

A notable feature was that the influence of ICCP was relatively minor for the low-alloy steel but still significant for the stainless steel alloys. These aspects demonstrate that, as in terms of TVL, there was a significant component of corrosive attack within the DIZ for stainless steels but not so for the low-alloy steel. The ICCP results also confirm the appreciable role of corrosive attack in the DIZ at higher salinities in that there are clearly measurable differences between the volume losses incurred at the highest salinity compared to those experienced when cathodic protection was applied.

Figure 5: DIZ volume loss of all tested materials in each salinity and ICCP

Table 4: Percentage increases in DIZ volume losses with increasing salinity for each test material

Test material	Percentage increase 0.05%NaCl → 3.5%NaCl	Percentage increase 3.5%NaCl → 10%NaCl
UNS S31600	15%	23%
UNS S15500	2%	30%
UNS G43400	9%	8%
UNS S32760	24%	10%

The volume losses in the outer area, VL_{OA} , are determined by subtracting the volume losses in the DIZ, VL_{DIZ} , from the total volume loss, TVL, as shown in Eq. 1.

$$VL_{OA} = TVL - VL_{DIZ} \quad \text{Eq. 1.}$$

These volume losses in the OA for all test materials in all test conditions are shown in Figure 6. Table 5 shows the percentage differences in OA material loss with increasing salinity for each test material. An interesting feature of the data in Figure 6 and Table 5 is that, whilst the OA volume losses for the stainless steels increase with solution salinity, there does not appear to be any significant benefit accrued from the

higher-alloyed stainless steel, UNS S32760. In some contrast, the OA material losses for the low-alloy steel follow a similar trend to the total volume losses (Figure 3) in that there is an increase from 0.05%NaCl to 3.5%NaCl but no further discernible OA material loss in the highest salinity solution. The percentage increases for OA material loss, shown in Table 5, demonstrate a generally similar trend to both TVL (Table 3) and DIZ (Table 4) material losses.

The material losses observed under ICCP conditions:

- again demonstrate that a substantial proportion of corrosive wear attack, on the low-alloy steel, occurs in the OA zone.
- are all measurably lower than found at the highest salinity for the stainless steels, thus replicating the trends observed in the DIZ.

Figure 6: OA volume loss of all tested materials in each salinity and ICCP

Table 5: Percentage differences in OA volume losses with increasing salinity for each test material

Test material	Percentage difference 0.05%NaCl → 3.5%NaCl	Percentage difference 3.5%NaCl → 10%NaCl
UNS S31600	4% increase	27% increase
UNS S15500	16% increase	23% increase
UNS G43400	242% increase	18% decrease
UNS S32760	17% increase	10% increase

3.3 Post-test microscopic observations

In order to obtain a deeper understanding of the degradation mechanisms and differences in the material losses caused by the effect of salinity on the different test materials under corrosive wear conditions, post-test surfaces were observed using a SEM. Figures 7 and 8 illustrate the typical damage observed for all materials and salinities; the post-test examinations on the SEM revealed two common features:

- in the DIZ (Figure 7), the sand particles have resulted in the formation of small impact craters caused by the particles directly impacting the material surface. As all test materials were engineering steels, the impacting sand particles cause plastic deformation of the ductile metallic surface, where the surface is indented at high impact angle, material is smeared to the lip of the impact crater. Continuing impacts have caused the surface to roughen due to the repeated plastic deformation and smearing of the ductile metallic material. Subsequently, the thin smeared material can be easily removed by the impacting sand particles [41, 42].
- in the OA (Figure 8), sliding abrasion damage marks are apparent, caused by sand particles impacting the test surface at low angles. This results in a cutting-type mechanism on the soft/ductile metallic material which causes it to plastically deform and smear in the direction of the flow of the impacting sand particles [4, 37].

Figure 7: Example post-test SEM image of typical impact crater and plastic deformation damage observed in DIZ; image shown of DIZ of UNS G43400 in 0.05%NaCl

Figure 8: Example post-test SEM image of typical sliding abrasion damage observed in OA; image shown of OA of UNS S15500 in 3.5%NaCl

A noticeable difference was observed between the OA of the low alloy steel compared to the stainless steels. Both corrosion pitting and sliding abrasion damage was evident in the low alloy steel, UNS G43400, in all test salinities (Figure 9a and 9c). However, for the stainless steels, sliding abrasion damage was only evident whilst corrosion pitting was absent, as demonstrated in Figure 9b.

Figure 9: Post-test SEM images of A - UNS G43400 OA in 0.05%NaCl; B - UNS S15500 OA in 10%NaCl; C - UNS G43400 OA in 10%NaCl

Figures 10 and 11 illustrate cross section images of the wear scars of UNS S15500 and UNS S 32760 respectively after FEC tests in 3.5%NaCl. The SEM images do not appear to be indicating any preferential wear on specific phases. Both wear scars demonstrate a sub-surface zone which is highly plastically deformed as a result of the impacting sand particles [43]. An additional, minor feature in Figure 11 is that the UNS S32760 alloy is also exhibiting sub-surface cracking. Semi-quantitative EDS analysis (Table 6) was conducted around the cracks and indicated that both the ferrite (spectrum 2 and 3 – greater Cr and Mo) and austenite (spectrum 1 and 4 – greater Ni) phases were present on either side of the crack. This potentially leads to the conclusion that the cracks may be occurring preferentially along phase boundaries. There was some indication of initiation of sub-surface micro-cracks in the UNS S31600 stainless steel after FEC tests but no such cracks were evident in the UNS S15500 alloy. It is felt that the sub-surface cracking was of such a small extent that it does not play a significant role in the overall erosive wear damage – which is dominated by the well-established results of severe plastic deformation.

Figure 10: Example of post-test SEM cross-sectional image of plastically deformed region in the DIZ of UNS S15500 after FEC test in 3.5%NaCl

Figure 11: Micro-cracking occurring at surface of UNS S32760 wear scar

Table 6: Semi-quantitative EDS analysis of phases observed in Figure 11

Spectrum	Si	Cr	Fe	Ni	Mo
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Spectrum 1	0.5	27	61	7.8	3.8
Spectrum 2	0.6	28	61	6.2	4.4
Spectrum 3	0	29	61	5.4	5.4
Spectrum 4	2.7	26	61	7.8	3.0

4. DISCUSSION

This work extends previous studies in this field [29, 30, 33, 35] which only evaluate low (circa. 0%NaCl) to intermediate salinities (circa. 3.5%NaCl). These studies [29, 30, 33, 35] demonstrate an increase in material loss with increasing salinity and a variety of interesting aspects have been observed by the present comparative study on engineering steels under corrosive wear conditions. A general aspect of the influence of salinity on corrosive wear is that increases in salt concentration are associated with more severe attack on all four alloys with exception to the behaviour of the low alloy steel under low angle corrosive wear. For this situation, there appears to be a substantial enhancement of damage in aqueous solutions containing 3.5%NaCl compared to the lowest salinity solution (0.05%NaCl) investigated, but the damage is not further exacerbated when the salt concentration rises to 10%NaCl. This feature mirrors other investigations of pure corrosion with salinity relationships [23, 28, 44]. Whilst detailed explanations of these trends are still unresolved, as argued by Sani et al. [23], in searching for a rationalisation of these corrosion rate/salinity trends, a simple correlation with the elevated electrical conductivity [32], and hence, increased corrosivity of saline solutions is unlikely to suffice. Additionally, it is difficult to rationalise a simple corrosion rate/electrical conductivity relationship with the observations of reduced deterioration rates at salt concentrations above approximately 3.5%NaCl. Alternative mechanisms that are considered in detail elsewhere [45] include:-

- the influence of salinity on the competition between adsorption of different anions, e.g. chloride and hydroxyl, in determining the progress of the anodic part of the overall corrosion reaction on low alloy steel [23, 24, 46].
- the influence of reduced dissolved oxygen concentrations at higher salinities [47] upon the oxygen reduction cathodic reaction.

The low-alloy steel (UNS G43400) has much greater corrosive wear damage across the range of salinities compared to the stainless steels due to its poor corrosion resistance, as has been observed in previous studies [3], 48]. This poor corrosion resistance stems from the absence of alloying elements in the metal matrix, such as chromium, which form passive films on the material surface, providing a physical barrier for corrosion reactions. The low-alloy steel was vulnerable to increased damage even in the 10%NaCl aqueous solution in the directly impinged regions, where mechanical erosive damage dominates.

Most studies into solid-liquid jet impingement employ a specimen that is much larger than the impinging jet diameter and report material losses of the entire specimen – like Figure 3 herein – which are, in essence, average material losses over the two zones, DIZ and OA. The advantage of the analytical approach [36] adopted in the current work is that it provides a means of assessing the behaviour of the two regions separately. This facilitates a more comprehensive understanding of the corrosive-wear material degradation processes involved during the impinging jet erosion-corrosion experiments. This is also a feature of many operational aspects when a slurry strikes particular regions of a component surface. In the present study, the influence of salinity upon the material loss of the low-alloy steel in the outer zone (Figure 6) follows the same general trend as that indicated by the overall measurements (Figure 3), but in the DIZ, the material loss appears to increase continuously with salinity (Figure 5). Moreover, the volume loss measurements on the directly-impinged zone have revealed that the resistance to pure erosion, i.e. when ICCP is applied, of the UNS G43400 steel is relatively inferior to that of the stainless steels. Additionally, the marginal superiority of the UNS S32760 alloy over the other stainless steels is attributed to its direct impingement erosion resistance and not with its sliding abrasion resistance. Also, the volumetric analysis technique demonstrated that most of the corrosion damage on the low alloy steel is in the OA, which is not evident from just assessing full sized specimens. These findings would not have been evident by only considering the total volume loss under CP conditions.

Turning to the behaviour of the stainless steel alloys studied in this work, in many circumstances (especially in the low impingement angle, OA), these materials exhibit considerably superior corrosive wear resistance compared to the low alloy steel, but are susceptible to higher material losses as the salinity is raised. This factor shows that the degree of erosion/abrasion domination, in the behaviour of the stainless steels, is reduced at the highest salt concentration. This also results in a reduced margin of superiority over UNS G43400 in the highest salinity solution, primarily in the DIZ. It is persuasive to attempt to link these observations to the roles of water salinity and stainless steel composition drawing on the well-established relationships relating these factors to the susceptibility of stainless steels to localised corrosion (pitting, crevice attack) via breakdown of the passive film due to increases in chloride content [49]. Such links have been suggested by others [50], but the following factors are also likely to be relevant:

- under solid-liquid erosion-corrosion conditions, periodic de-passivation and re-passivation occur [4, 37, 40]
- the influence of erosive damage to passive films on the progress of the oxygen reduction cathodic reaction [45]

Of all the tested materials, the superduplex stainless steel (UNS S32760) performed the best in terms of the lowest TVL and DIZ volume loss in every test condition. This is not surprising since it is the most corrosion resistant stainless steel investigated in this study, with the highest proportion of alloying

elements encouraging the formation of more stable passive films. However, this observation was not evident in the lack of improved performance of UNS S32760 in the OA.

The application of cathodic protection provided a substantial reduction in material loss on the low alloy steel but demonstrated that the erosion-corrosion damage on the stainless steels also involved a significant contribution of corrosion-related damage, even under high-angle impingement where the damage is typically erosion dominated.

Another interesting aspect of the study demonstrated that there were no clear relationships between material hardness and corrosive wear resistance. Some studies in the past have shown that there are relationships between abrasive wear and hardness [51, 52]. However, in this study, the material with the lowest hardness (austenitic stainless steel - UNS S31600) has similar pure mechanical material losses compared to the material with the greater hardness of the tempered martensite alloys (UNS G43400 and UNS S15500) in low angle impingement conditions. A plausible explanation for this is work hardening effects caused by the sand particles impacting at low angles and also austenite to martensite transformation which has been observed in other studies [53, 54]. The improved erosion-corrosion resistance of UNS S32760 (Superduplex stainless steel – ferrite/austenite microstructure) is likely to be associated with both its high corrosion resistance as well as its potential to work harden due to the presence of the austenite phase [55]. It is likely that correlations between hardness and wear resistance only apply in relation to specific groups of materials with similar microstructures.

5. CONCLUSIONS

1. This study showed that increasing the salinity from 0.05%NaCl (freshwater) to 3.5%NaCl (mimicking seawater) substantially increased the corrosive wear damage of UNS G43400. However, as the salinity was increased from 3.5%NaCl to 10%NaCl ("brine"), there was no additional volume loss. Volumetric analysis revealed that the majority of the increase in volume loss compared to freshwater originated from the OA, of which a significant proportion was corrosion-related damage equating to 36%, 82% and 78% of the total OA volume loss in freshwater, seawater and brine solutions respectively. These findings indicate a good correlation between corrosive-wear deterioration and pure corrosion trends reported in the literature.
2. The stainless steels, in many circumstances, exhibited much lower sensitivity to solution salinity than the low alloy steel in terms of corrosive wear. Nevertheless, it was notable that, in the DIZ, there was a significant contribution of corrosion-related damage to the total material loss. In the most severe situations – the most-saline water in the directly-impinged zone – the margin of superiority of the two lower-grade stainless steels over the low-alloy steel was significantly

compromised. However, the superduplex stainless steel maintained its advantage over the low alloy steel.

3. The directly-impinged zone of specimens was erosion-dominated. Nevertheless, for all four materials there was a consistent trend of increased material loss with solution salinity.
4. One noticeable feature was the observed differences in effects of salinity on material loss for the low alloy steel in the DIZ (continual increase) compared to the material loss in terms of TVL and OA in line with measurements of pure corrosion rates in previous studies, where material losses were observed to increase from circa 0%NaCl to circa 3.5%NaCl before decreasing.
5. Cathodic protection significantly improved the performance of the low alloy steel with total volume loss reductions of up to 70%, to the extent of substantially reducing the 'deficit' of this steel compared to the stainless steels. Cathodic protection provided little benefit to the stainless steels in freshwater (2-4% TVL reduction) but noticeably reduced the damage at higher salinities, providing at least 25% TVL reduction at 10%NaCl. This again is a demonstration of the significant role of corrosion-related damage on nominally corrosion-resistant materials.
6. In all test conditions investigated in this study, there was no evidence of a direct correlation between material hardness and material loss.

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