Analysis of mechanical and chemical mechanisms on cavitation erosion-corrosion of steels in salt water using electrochemical methods

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Cavitation erosion-corrosion causes damage and removal of material especially in rotors of centrifugal pumps, water turbines, as well as in control valves and in motors. Based on a dynamic corrosion model the pure mechanical erosion amount of different steel alloys was identified using an indirect cavitation test method combined with an electrochemical cell. We demonstrate that cavitation erosion can be enormously reduced by application of external cathodic potentials. The cavitation rate was in-situ determined using atomic emission spectrometry during the cavitation test. Due to the separately identified pure mechanical and the combined corrosive and synergistic cavitation erosion-corrosion correlation with hardness and arising charge densities during cathodic potentials were found for the mechanical part.

Keywords: Cavitation erosion-corrosion; In-situ erosion monitoring; Electrochemistry

1. Introduction

Cavitation is the formation and dissolution of vapour or gas filled pockets inside the flow of liquids [1, 2]. The collapse of bubbles on a surface causes fluid microjets that are directed against the surface and lead to severe deterioration and surface material loss as these microjets generate extreme pressure and temperature peaks. The most common sources of cavitation in technical applications are fast moving objects in a fluid such as rotors of centrifugal pumps, water turbines, lubricants in piston rings and bearings, control valves, spillways, engines, propellers and in the renewable energy sector at tidal stream turbines [3]. In addition, cavitation can be responsible for the occurrence of noise due to vibrations and a loss of energy efficiency. Due to its economic impact prevention and control of cavitation erosion has been studied extensively [4-8].

In this context the cavitation erosion of stainless steel [5] and the effect of temperature, pH and sulphide [6] were investigated. It was found that the cavitation erosion behaviour strongly correlates with mechanical properties of metals [7]. An overview of scientific work in this field is given by Karimi and Martin [8].

Furthermore the superposition of mechanical erosion and electrochemical corrosion is assumed as a main degradation mechanism for cavitation engineering alloys in corrosive environment [9]. Therefore synergistic mechanisms of cavitation and corrosion have to be
taken into account. Erosion-corrosion interactions have been studied for carbon steel [10], pure iron [11] and cast iron [12]. Many publications focus on the investigation of synergistic effects of erosion and corrosion for different fluids (acidic slurry medium, seawater) and materials (various engineering alloys, copper, cuprous-nickel, marine and offshore materials) [13-19]. The role of different parameters influencing erosion-corrosion was identified by the work of Rajahram et al. [20, 21]. Cavitation erosion-corrosion tests to identify inhibitory mechanisms for iron in a 3 % sodium chloride solution were conducted by Oka and Ohkubo [22]. In addition, laser surface modification of stainless steels was used to increase their electrochemical corrosion resistance and cavitation erosion-corrosion resistance [23], [24].

Electrochemical measurements are applicable to investigate specific material parameters as the passivation of stainless steel in more detail [25]. In-situ electrochemical measurements during solid particle impingement were carried out to investigate the influence of passivation and repassivation [26]. It was found that higher measured current levels were associated with damage of the passivating film which limits repassivation and contributes to enhanced corrosion. Also dynamic impedance spectroscopy was used to evaluate the cavitation erosion-corrosion degradation of mild steel [27]. The effect of applied potential on passivation and erosion–corrosion of a Fe-based amorphous metallic coating under slurry impingement was evaluated by Zheng et al. [28]. The impact of oxide films on a steel surface on wear was also investigated using an impact-fretting tribometer in combination with electrochemical methods [29]. Nie et al. [30] investigated the corrosion behaviour of metallic materials in ethanol-gasoline alternative fuels using cyclic potentiodynamic tests. They found a higher anodic Tafel slope using ethanol as electrolyte as than using NaCl. This behaviour is caused by a film formation on the surface, which is less permeable and can even obstruct the metal dissolution reaction, but still permits the electrochemical reaction. Differences in the corrosion kinetic of the different steel materials arise in connection to the microstructure. For example large Si particles cause more cathodic reaction on the surface and involve higher corrosion current density and lower polarization resistance. It was pointed out that the corrosion resistance increases with the measurement of a more positive corrosion potential (better passivity) and a higher polarization resistance ($R_p$).

Burson-Thomas and Wood [31] reviewed the developments in erosion–corrosion over the past 10 years and found that the research focus was the investigation of synergistic effects of erosion and corrosion, application-specific studies (marine, oil and gas engines and automobile industry) and Fe-based materials, Ni-based alloys and hard metal coatings. But they also mentioned the current lack in understanding the fundamental mechanisms in erosion–corrosion which should be examined using mechano-electro-chemical techniques. A review about physical mechanisms for cavitation erosion loads and an overview of cavitation erosion models is given by Terwisga et al. [32]. This work is based on this problem as the approach consists of the coupled investigation of cavitation erosion and electrochemical methods. The hypothesis of this work is that the influence of corrosion on cavitation erosion can be evaluated and reduced by applying electrochemical potentials. In particular, electrochemically applied cathodic electrochemical potentials lead to a suppression of corrosion reactions thus enabling the quantification of the corrosive attack in cavitation. Preliminary work using ionic liquids (ILs) [33], aqueous solutions of ILs [34] and sodium chloride [35], demonstrated the effect of electrochemical potentials, applied in a three-electrode configuration [36], on the tribological behaviour. Therefore the objective of this work is to characterise erosion mechanisms of corrosion and cavitation erosion using electrochemical methods.
2. Experimental

2.1 Materials

The cavitation erosion behaviour of steel 1.3505 (DIN 100Cr6, AISI 52100), tempered 1.3505T (heat treatment according to DIN EN ISO 683-17) and 1.4125 (DIN X105CrMo17, AISI 440C, annealed condition) was analysed using different techniques. The samples had a circular cross-section of 24 mm in diameter and a height of 7.9 mm. Surface near micro-hardness (nanoindenter Fischerscope H100C, Helmut Fischer GmbH, according to ISO 14577) and macro-hardness (Vickers HV2) of the three different steels were measured (Table 1). Roughness and after cavitation tests erosion profiles were characterised using profilometry (Hommel Tester T8000, Co. Jenoptik). Mass loss due to cavitation was measured using precision balance (Sartorius R160 P). Sample topology after cavitation was analysed with scanning electron microscope equipped with energy dispersive X-ray spectroscopy for determination of oxygen content (SEM, S-3400N, Co Hitachi). In addition, chemical composition on the surface and the bulk material was measured using XPS (X-ray photoelectron spectroscopy, Leybold MAX 100; argon ion sputtering, sputter rate: 2 nm/min; 1 kV; 500 nA). The microstructure was analysed by structural analysis after polishing and etching of the steels using light microscope.

Table 1
Chemical composition and mechanical properties of specimen materials

<table>
<thead>
<tr>
<th>Material</th>
<th>1.3505</th>
<th>1.3505T</th>
<th>1.4125</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_a$ (µm)</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>$R_z$ (µm)</td>
<td>0.36</td>
<td>0.37</td>
<td>0.46</td>
</tr>
<tr>
<td>Specimen area, $A_0$ (mm²)</td>
<td>452</td>
<td>452</td>
<td>452</td>
</tr>
<tr>
<td>Vickers-hardness HV2</td>
<td>167</td>
<td>631</td>
<td>226</td>
</tr>
<tr>
<td>Micro-hardness HV0.031</td>
<td>245</td>
<td>995</td>
<td>380</td>
</tr>
<tr>
<td>Micro-Young’s Modulus (GPa)</td>
<td>218</td>
<td>228</td>
<td>235</td>
</tr>
<tr>
<td>Electrochemical equivalent, $K$ (g/A s)**</td>
<td>2.85 x10⁻⁴</td>
<td>2.85 x10⁻⁴</td>
<td>2.68 x10⁻⁴</td>
</tr>
<tr>
<td>Density, ρ (g/cm³)</td>
<td>7.79</td>
<td>7.68</td>
<td>7.65</td>
</tr>
<tr>
<td>C1s.Carb (wt.%)***</td>
<td>9.38</td>
<td>2.95</td>
<td>2.85</td>
</tr>
<tr>
<td>O (wt.%)**</td>
<td>2.28</td>
<td>5.25</td>
<td>0.69</td>
</tr>
<tr>
<td>Si (wt.%)<em>Ü</em>**</td>
<td>-</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>Cr (wt.%)**</td>
<td>3.16</td>
<td>1.59</td>
<td>31.26</td>
</tr>
<tr>
<td>Mn (wt.%)*</td>
<td>0.24</td>
<td>0.33</td>
<td>0.4</td>
</tr>
<tr>
<td>Mo (wt.%)**</td>
<td>-</td>
<td>-</td>
<td>1.04</td>
</tr>
</tbody>
</table>

*tanpered according to DIN EN ISO 683-17; **calculated using formula from [37], ***measured with XPS at a sputter depth of 50 nm

2.2 Electrochemical measurements

Electrochemical measurements were carried out with an electrically insulated 3-electrode test setup using a potentiostat Parstat4000 (Co. Ametek) in 0.6 M NaCl (≈ seawater) solution (Figure 1). As reference electrode (RE) Ag/AgCl (Ø 4 mm, standard potential against a standard hydrogen electrode: -194 mV, Co. Warner Instruments) and counter electrode (CE) platinum were used. The particular examined steel specimen was set as working electrode (WE) with a contact area $A_0$ with the electrolyte of 452 mm². Three different measuring methods were applied to analyse the static and dynamic corrosive behaviour of the steel types. At first the open circuit potential (OCP) was measured before starting the cavitation
tests. The dynamic potential method (DPM) was used to characterise the static corrosion coefficient $C_0$ which describes the conditions without external mechanical impact. It was found by Iwabushi et al. [38] that the corrosion rate at the fresh surface (without passive layer), as it occurs under mechanical action (i.e., sliding friction), is higher than at static conditions. This corrosion behaviour can be estimated by the current density obtained from the potential pulse method PPM. Dynamic corrosion, the predominated damage mechanism during cavitation erosion, was therefore analysed using PPM, as this measurement represents the corrosion behaviour for the fresh surface [38]. The test procedure was conducted as following:

1. **DPM:** 60 min measuring OCP, polarization curve between -500 mV to 500 mV vs. OCP, scan rate: 0.1 mV
2. **PPM:** 60 min measuring OCP, polarization curve between -500 mV to 500 mV vs. OCP, scan rate: 1000 mV/s

The most important electrochemical parameters obtained from the polarization curves (Tafel plots) were the corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and the anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$). On the basis of these values the corrosion rate per year ($m_y$ in mm/year, eq. 1) was calculated. Whereas the molar mass ($M$), the number of electrons which participate at the chemical reaction ($z$), the Faraday constant ($F = 96485.309 \text{ A} \cdot \text{s/M}$), the time (one year, $t = 3.15 \times 10^7 \text{ s}$) and the density ($\rho$ in g/cm$^3$, values see Table 1) are given parameters. The equivalent weight ($Q$, eq. 2) for alloys which is the ratio of atomic weight of the element and the number of electrons required to oxidize an atom of the element in the corrosion process is calculated according to ASTM G102 – 89(2015)e1. Each measurement was carried out at least three times.

$$m_y = \frac{M \cdot i_{corr} \cdot t}{z \cdot F \cdot \rho} \quad \text{(1)}$$

$$Q = \sum \frac{n_i \cdot f_i}{W_i} \quad \text{(2)}$$

Where $f_i$ is the mass fraction of the $i^{th}$ element in the alloy, $W_i$ the atomic weight of the $i^{th}$ element in the alloy, and $n_i$ the valence of the $i^{th}$ element of the alloy.

### 2.3 Cavitation tests

Cavitation tests were performed on the basis of the indirect vibratory method according to ASTM G32-10 [39] in the 3-electrode test setup (Figure 1). Each cavitation test was carried out at least three times. An ultrasonic device UP200St (Co. Hielscher) was used in combination with a titanium sonotrode ($\varnothing 7.0 \text{ mm} = 38.5 \text{ mm}^2$). The immersion depth was 12 mm and the distance between sonotrode and steel sample 0.6 mm. Tests were carried out at a frequency of 26 kHz with an amplitude of 150 µm within a circulating and to 25 °C tempered 0.6 M NaCl solution. Tests which represent the cavitation erosion behaviour at real technical conditions were conducted without an external potential (OC: open circuit). An external cathodic potential was applied to analyse changes in the corrosion and damage mechanisms. The cavitation tests were carried out in following way:

1. **OCP:** 10 min measuring OCP without cavitation, 2 h cavitation test at OC, OCP measuring for 10 min
2. **Cathodic:** 10 min measuring OCP without cavitation, 2 h cavitation test at -500 mV vs. OCP, OCP measuring for 10 min
2.4 Analysis of cavitation erosion

The test samples were weighted before and after the cavitation test to determine the material loss in relation to the applied cavitation loads, potential and used steel. The mass loss is converted to a cavitation volume and a mean depth of erosion (MDE) using following equation [40]:

\[
MDE = \frac{10 \cdot \Delta W}{\rho \cdot A_W} \tag{3}
\]

where \(A_W\) is the cavitation area (cm²), \(\Delta W\) the mass loss (mg) and \(\rho\) the density (g/cm³) of the tested material. In addition, the cavitation area was characterised with an optical microscope (VHX-500F, Co. Keyence Corporation) and additionally analysed using SEM/EDS (S-3400N, Co. Hitachi). The worn profiles of the cavitation areas were additionally measured by tactile scanning of the surface (Wave System T8000, Co. Hommelwerke). The cavitation rate was determined from the slope increase of the iron concentration in the water, which was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). This technique is suitable to measure lowest fraction of iron within the 0.6M NaCl solution during cavitation test.

3. Tribocorrosion and dynamic corrosion model

Mischler and many other authors [41-44] explained that in a tribological contact physico-chemical and mechanical surface impact cause irreversible transformations of material. This behaviour is called tribocorrosion which changes the lubrication, erosion and corrosion characteristic of a tribological system. Therefore total erosion removed by tribocorrosion consists of mechanical and chemical parts, whereas synergistic effects can result in accelerated material removal [44]. For example, the removal of passive film on stainless steel due to abrasion leads to more severe corrosion of the underlying reactive, bare material [43]. Other corrosion–erosion interaction can also result in surface films which protect the metal from erosion [43]. Tribocorrosion was investigated using electrochemical methods [42] to analyse the tribocorrosion of passive metals [45, 46] the acceleration of tribocorrosion [41], and the interplay between chemical, electrochemical, and mechanical reactivity of surfaces [47]. Furthermore tribocorrosion of passive metals in the mixed lubrication regime was investigated based on a mechanistic approach [44]. Vieira et al. found that the open circuit potential (OCP) during rubbing shifts due to the formation of a galvanic coupling [43]. They measured a cathodic shift of potential during tribocorrosion of passive metals which is caused by this galvanic coupling between the mechanically depassivated areas (anode: metal oxidation dominating electrochemical reaction, metal dissolution and if possible re-growth of passive film) and the surrounding passive areas (cathode reduction of water and/or oxygen). The emerging electrons on the anode flow through the metal and are consumed by the reduction reaction that also occurs on the anode. This leads to generation of galvanic ionic current that flows from the anode through the solution. The anodic and cathodic current
are equal in a galvanic cell and therefore the measured change of electric potential due to
tribological impact results from the balance of the anodic and cathodic current as [43]:

\[ A_a \cdot I_a + A_c \cdot I_c = 0 \]

Here A is the area and I the current density at anodic and cathodic condition. But it must be
noticed that local variations of current densities occur due to material deformation. In
addition, an ohmic drop (\( R_{\text{ohm}} \): ionic resistance of solution between cathode and anode) in the
solution leads to a difference between cathodic and anodic potential. The cathode potential
in the galvanic coupling depends mainly on two factors: the anodic current and the anode to
cathode area ratio. Theoretically there exist two limiting theoretic galvanic coupling situations
[43]:
- completely depassivated erosion track: galvanic coupling between the negative
charged erosion track and the positive area surrounding it (Figure 2)
- incompletely depassivated erosion track: still passive areas within the erosion track
and therefore short range galvanic coupling on the worn area and the area directly
aside the erosion track

Since it was found by Sato et al. [48] that the removal efficiency of oxides is 100 % under
fretting-impact we also assume that under cavitation erosion no depassivation/repassivation
processes (no re-growth of the passive film) occur and a completely depassivated erosion
track exists. Under tribological conditions the \( \frac{A_a}{A_c} \) ratio increases significantly due to
erosion.

As mentioned in literature, especially the deterioration of the protecting passive layer plays a
major role in the synergistic mechanisms at cavitation erosion. Due to mechanical or
cavitation stresses caused by cavitation, sliding or impingement, passive films are destroyed
[49, 50]. Surfaces without protective layer exhibit very high chemical activity, thus severe
corrosion occurs under external stress. A dynamic corrosion model published by Iwabuchi et
al. describes the corrosion and erosion mechanisms of fresh metal surfaces formed by
scratching and sliding [38, 51]. Within this model the erosion volume \( W \) is composed of the
mechanical erosion \( M_0 \), static corrosion volume \( C_0 \) and the synergistic factor \( \Delta W \), where \( W_d \)
is called the dynamic corrosion factor [48, 51, 52]:

\[ W = M_0 + C_0 + \Delta W = M_0 + W_d \]

In this model, the superposition between mechanical erosion and corrosion are crucial.

As schematically shown in Figure 2a, cavitation erosion leads to removal of the protecting
oxide layer which can be seen as an analogy to mechanical erosion (\( M_0 \) in eq. 5). From this
point the fresh surface is exposed and dynamic corrosion predominates the removal
behaviour (Figure 2b). These values can be evaluated quantitatively from the experimental
results. Therefore the main hypothesis of this work is the assumption that externally induced
cathodic electrochemical potentials prevents static and dynamic corrosion. Consequently,
pure mechanical erosion \( M_0 \) can be quantified with cavitation tests at cathodic potential.
Without inducing external potentials, but measuring the resulting OCP during cavitation, \( W_{\text{cav}} \)
can be measured. The area directly influenced by cavitation basically acts as anode due to
the exposure of the fresh surface and the surrounding area acts as cathode on the specimen
(Figure 2c). Then the whole area \( A_0 \) of the tested specimen can be calculated:

\[ A_a + A_c = A_0 \]
By combining equation (4) and (6) the anodic area in the dynamic corrosion is obtained as:

\[ A_a = \frac{I_c \cdot A_0}{I_a - I_c} \]
4.2 Corrosion behaviour

In Figure 5 the change of open circuit potential (OCP) with time is shown. During the first 15 min the open circuit potential (OCP) decreases to a relatively stable value for the three tested steel alloys (Figure 5a). This characteristic is typical for corroding systems. Stainless steel 1.4125 exhibits the most positive OCP value after 60 minutes testing time. Based on these OCP values the potentiodynamic polarization tests were carried out for each steel using dynamic potential method (DPM, 0.1 mV/s) and potential pulse method (PPM, 1000 mV/s). The results show that the corrosion current density ($i_{\text{corr}}$) of PPM is more than one order of magnitude larger than that of DPM using the two unhardened materials (Figure 5b and 5d). Using hardened 1.3505 there is even a difference of 6 orders of magnitudes for $i_{\text{corr}}$ between DPM and PPM (Figure 5c). This difference results from the fact that current density at PPM can be regarded as the corrosion property of the fresh exposed
surface. In addition, the corrosion potential \( (E_{\text{corr}}) \) decreases for all tested materials at PPM measurement. This indicates a secondary loss of its corrosion-resistance properties under dynamic corrosion conditions. In addition, the anodic Tafel slopes \( (\beta_a) \) are higher at PPM which indicates a faster reaction (oxidation of metal) with change of potential. Based on these electrochemical measurements the corrosion rate per year was calculated. All measured and calculated values of the electrochemical analyses are listed in Table 2. In case of steel 1.4125 the passive layer gets removed at high scan rate which strongly increases the corrosion behaviour. Steel 1.3505 shows nearly the same behaviour and even a more pronounced increase using the hardened type. This could be related to differences in the microstructure as shown by Nie et al. [30], since 1.3505T has a fine grained martensitic microstructure in contrast to the other steels with many undissolved chromium carbides compared with a thick oxide layer. These results show that the corrosive characteristics of the tested steels become more important and distinctive using the PPM where the surface is permanently activated as it occurs during cavitation.

**Figure 5:** Electrochemical measurements in 0.6 M NaCl solution: Results of open circuit potential (a) and potentiodynamic tests without cavitation at different scan rates (0.1 mV/s and 1000 mV/s) using steel 1.4125 (b), 1.3505T (c) and 1.3505 (d).

**Table 2**
Corrosion parameters obtained from electrochemical measurements with DPM and PPM in 0.6 M NaCl solution for the three steel types

<table>
<thead>
<tr>
<th>Material</th>
<th>1.3505</th>
<th>1.3505T</th>
<th>1.4125</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCP (mV)</td>
<td>-659 ± 7</td>
<td>-605 ± 16</td>
<td>-556 ± 7</td>
</tr>
<tr>
<td>Q (g/M)</td>
<td>26.88</td>
<td>26.88</td>
<td>24.42</td>
</tr>
<tr>
<td>( i_{\text{corr}} ) (A/cm²)</td>
<td>1.39E-4 ± 5.73E-5</td>
<td>9.20E-09 ± 3.97E-09</td>
<td>6.16E-05 ± 2.51E-05</td>
</tr>
</tbody>
</table>
4.3 Cavitation tests at open-circuit and cathodic potential

At the start of the cavitation test there is an instant increase of the OCP (=15 %) to more positive values for the two 1.3505 types (Figure 6a). This potential change results from the balance of the anodic current and cathodic current as described in eq. 4. This rapid change of OCP is caused by depolarization of the cathode and increasing corrosion due to an enhancement of the anodic reaction. In addition, such shifts can also be caused by the damage of thin layers of corrosion products on the sample surface. Therefore, this shift of the OCP can be attributed to an increasing mass transport induced by cavitation bubbles [27]. In contrast, there is no considerable OCP change for the stainless steel (Figure 6a). During cavitation test the OCP is constant for all tested steels. The drop in potential after cavitation test is taken as an evidence for instantly decreasing corrosion after finishing the cavitation test for all tested steels. The cathodic potential of -500 mV vs. OCP was very stable during potentiostatic cavitation tests (Figure 6b). After the cavitation test, the initial potential was immediately restored. The required current density to induce the cathodic potential was quite stable during cavitation test with a slight increase during the first 15 min since the oxidation current becomes larger (Figure 6c). This increase arises due to erosion accelerated corrosion as the depassivated areas contribute to the material damage. The calculated corresponding charge densities (integration of current over time) are illustrated in Figure 6d. The highest amount of charge density was observed in the tests using steel 1.3505.
4.4 Mass loss measurements

After cavitation test the mass loss of the samples was measured using a precision balance to quantify different occurring erosion mechanisms. In addition, the cavitation area was quantified to calculate the mean depth of erosion (MDE). Though tests without external potential represents the cavitation erosion caused by mechanical, corrosive and synergistic effects \( W_{\text{cav}}=W_0+C_0+\Delta W \) as it appears in real applications. In contrast, at external cathodic potential cavitation, erosion damage is only attributed to mechanical impact. Thus the difference in cavitation erosion between these two test conditions is assigned to corrosive and synergistic effects. As illustrated in Figure 7a higher hardness results in lower MDE for steel 1.3505 after cavitation test. On contrast, steel 1.4125 despite a lower hardness exhibits the lowest erosion loss. This result can be explained by comparing the influence of corrosive and synergistic effects, which cause 77% (unhardened) and 100% (hardened) of the mass loss of the 1.3505 steels and only 35% for the stainless steel 1.4125. Conversely, pure mechanical material removal is predominant for the stainless steel, whereas this damage mechanism can be neglected for the hardened steel 1.3505. The corresponding values for MDE, cavitation mass loss and volume are listed in Table 3. The calculated MDE values are significantly higher than for special HVOF-sprayed novel Fe-based alloy coatings (MDE≈5 µm after 2 h) as shown by Milanti et al. [40]. But at cathodic potential it is possible to realize similar or even better MDE values for normal non-optimized steel. Figure 7b illustrates the increase of iron content during cavitation test using steel 1.4125 at OC. The cavitation rate at OC decreases from initially 0.038 mg/min to 0.015 mg/min (≈40% of initial cavitation rate) from 25 to 60 min and decreases further to 0.004 mg/min (≈10% of initial...
cavitation rate) during the second hour of cavitation test. This decrease in the cavitation may results due to filling of pits by a liquid which reduces the intensity of cavitation load.

Figure 7: Cavitation erosion quantification of the three different steels after cavitation test in 0.6 M NaCl solution (26 kHz, 150 µm, 25 °C, 2 h): (a) Comparison of mean depth of erosion (MDE) at open circuit (OC without external potential → M₀ + C₀ + ΔW), at cathodic potential (-500 mV vs. OCP → M₀) and its difference (Δ → C₀ + ΔW); (b) Determination of erosion rates (linear polynomial fit) by measuring iron content increase using ICP-OES measurement during cavitation test with steel 1.4125 at open circuit without external potential (OC).

Table 3
Results of mass loss after cavitation test (0.6 M NaCl, 26 kHz, 150 µm, 25 °C, 2 h)

<table>
<thead>
<tr>
<th>Material</th>
<th>1.3505</th>
<th>1.3505T</th>
<th>1.4125</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₀ (mm³)</td>
<td>0.342 ± 0.037</td>
<td>0</td>
<td>0.156 ± 0.023</td>
</tr>
<tr>
<td>M₀ (mg)</td>
<td>2.6 ± 0.3</td>
<td>0</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>MDE₀ (µm)</td>
<td>9.8 ± 1.1</td>
<td>0</td>
<td>4.9 ± 0.7</td>
</tr>
<tr>
<td>W_cav.,meas. (mm³)</td>
<td>1.464 ± 0.290</td>
<td>0.651 ± 0.027</td>
<td>0.242 ± 0.014</td>
</tr>
<tr>
<td>W_cav.,meas. (mg)</td>
<td>11.1 ± 2.2</td>
<td>4.9 ± 0.2</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>MDE_cav. (µm)</td>
<td>44.0 ± 8.7</td>
<td>20.1 ± 0.8</td>
<td>8.1 ± 0.5</td>
</tr>
<tr>
<td>C₀ + ΔW (mm³)</td>
<td>1.122 ± 0.328</td>
<td>0.625 ± 0.027</td>
<td>0.086 ± 0.037</td>
</tr>
<tr>
<td>C₀ + ΔW (mg)</td>
<td>8.5 ± 2.5</td>
<td>4.8 ± 0.2</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>MDE₀+C₀+ΔCM (µm)</td>
<td>33.7 ± 9.8</td>
<td>19.3 ± 0.8</td>
<td>2.9 ± 1.3</td>
</tr>
</tbody>
</table>

Cavitation tests can be used to determine the total erosion, the pure mechanical erosion and the total corrosive erosion. The higher chromium content of stainless steel 1.4125 has a positive effect and the corrosive erosion portion is significantly reduced in contrast to 1.3505. In this case, mechanical erosion predominates against the corrosive erosion. Mechanical erosion of the stainless steel also results from its relatively low hardness. In contrast, the hardened steel 1.3505ST shows only corrosive erosion and no mechanical erosion. The differences in the corrosion of the two 1.3505 steels may be explained by the different microstructures since the tempered steels has finer undissolved chromium carbides and a thicker oxide layer. There is no direct relation between hardness and total erosion due to the influence of corrosive effects. Contrary at cathodic polarisation that suppresses corrosive attack, hardness correlates with the mechanical amount of erosion volume (Figure 8a). But it must be noticed that high material hardness provides a long incubation period. At the end of this period, hard materials typically exhibit higher cavitation erosion rate than materials with lower hardness. This situation can also occur using 1.3505ST steel. In order to more accurately determine the current flow of the materials, the electrical charge density is calculated at cathodic polarisation (from Figure 8a). As shown in Figure 8b there is no
correlation between erosion volume and charge density transfer. Since the charge density transfer is dependent on the electric conductivity, different steel grades must be considered separately, because structural changes and alloying elements influence the electrical conductivity. In order to establish a relation, further tests and measurements are necessary.

Figure 8: (a) Mechanical part of cavitation erosion is strongly connected to hardness in contrast to total erosion. (b) Mechanical part of cavitation erosion increases as charge density is higher.

4.5 Erosion characteristics

The worn areas investigated using digital light microscope after cavitation test are illustrated in Figure 9. The radial color changes at the outer boundary of the cavitation areas indicate differently strong erosion leading to changing flow characteristics of the liquid. It has been shown in literature that cavitation erosion occurs most intensively in the transition to laminar flow [28]. The erosion profile of the cavitation area of 1.3505 at OC and cathodic potential measured using stylus profilometry is shown in Figure 9c. It can be seen that the highest amount of material loss occurs in the centre of the cavitation area.

Scanning electron microscopy (SEM) was used to make high-resolution images of the cavitation surfaces (Figure 10). With the hardened steel 1.3505T, relatively smooth surfaces are visible after cavitation, which indicates low erosion. Using stainless steel 1.4125 and steel 1.3505, heavily jointed erosion patterns were observed after the cavitation tests, which indicate a high surface roughness and high erosion. The high surface roughness under cavitation erosion further intensifies the corrosion degradation of the material, since the assailable surface area increases.

The change of surface roughness before and after cavitation is illustrated in Table 4. There is only a slight change of roughness after cavitation using hardened steel 1.3505T. In contrast, roughness significantly increases for steel 1.3505 and the stainless steel, whereas steel 1.4125 shows less difference related to the applied potential.

Table 4
Change of roughness after cavitation test

<table>
<thead>
<tr>
<th>Material</th>
<th>Roughness</th>
<th>1.3505</th>
<th>1.3505T</th>
<th>1.4125</th>
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<tr>
<td></td>
<td>$R_a (\mu m)$</td>
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<td>0.04</td>
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<tr>
<td></td>
<td>$R_z (\mu m)$</td>
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<td>0.37</td>
<td>0.46</td>
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<td></td>
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<tr>
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<td>0.07</td>
<td>3.09</td>
<td></td>
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<tr>
<td></td>
<td>14.41</td>
<td>0.51</td>
<td>15.81</td>
<td></td>
</tr>
<tr>
<td>-500mV vs. OCP</td>
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<td>0.07</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.41</td>
<td>0.51</td>
<td>15.81</td>
<td></td>
</tr>
<tr>
<td>ΔOCP/-500mV vs. OCP</td>
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<td>-0.02</td>
<td>0.40</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>$R_z$ (µm)</td>
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<td>-0.27</td>
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<td>ΔOCP/-500mV vs. OCP</td>
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</tr>
<tr>
<td></td>
<td>$R_z$ (%)</td>
<td>-39%</td>
<td>-35%</td>
<td>6%</td>
</tr>
</tbody>
</table>

**Figure 9:** Erosion analysis using optical microscope after cavitation test (0.6 M NaCl solution, 26 kHz, 150 µm, 25 °C, 2 h) of the three different steels at OC (a) and externally induced cathodic potential (b); Erosion profile measured using profilometer of the cavitation area of 1.3505 (c), 1.3505T (d) and 1.4125 (e) at OC and cathodic potential.
Conclusions

We developed an indirect cavitation test method combined with an electrochemical cell to influence and measure the cavitation erosion-corrosion of steel 1.4125, 1.3505 and tempered 1.3505T in 0.6 M NaCl solution at room-temperature.

Electrochemical investigations revealed that an activated free surface exhibits a much higher corrosion current density accompanied with a corrosion potential drift to a more negative value. In addition, the corrosion behaviour at static conditions is much smaller for 1.3505T due to the microstructure with its fine undissolved chromium carbides combined with an oxide layer.

The mean depth of erosion (MDE) can be reduced with cathodic potentials by 36 % (1.4125), 77 % (1.3505) and almost completely for steel 1.3505T compared to open circuit. Using this technique it was demonstrated that corrosive and synergistic mechanisms have higher impact on erosion for steels 1.3505 than pure mechanical damage. In contrast, for stainless steel 1.4125 we found a contrariwise erosion behaviour since mechanical damage is higher than corrosive and synergistic. Thus a correlation between pure mechanical erosion and hardness was found.

Using ICP-OES erosion rate was measured in-situ during cavitation test by determining increasing iron content. It was proven that the erosion rate decreases with advancing test duration using steel 1.4125 at open circuit without external potential.

With focus on applications cathodic potentials could be induced galvanically by specific material combinations that no external potentials have to be applied as recently shown in friction tests to reduce wear [53].
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References


Graphical-abstract

Highlights

- Combination of cavitation tests with electrochemical methods.
- Identification of pure mechanical damage mechanisms.
- Enormously reduction of cavitation erosion using external cathodic potentials.
- Both alloying constituents and hardness influence the cavitation behaviour.
- In-situ determination of cavitation rate using atomic emission spectrometry.