

Erosion wear of vinylester matrix composites in aqueous and acidic environments at elevated temperatures

Reija Suihkonen¹, Mari Lindgren², Sanna Siljander¹, Essi Sarlin¹, Jyrki Vuorinen¹

¹Tampere University of Technology, Department of Materials Science, P.O. Box 589, FI-33101 Tampere, Finland

²Outotec Research Center, P.O.Box 69, FI-28101 Pori, Finland

ABSTRACT

Slurry erosion wear performance of glass fibre reinforced vinylester composite (FRP) has been studied using a pilot-scale erosion test apparatus. Tests were conducted at elevated temperatures in aqueous and acidic environments. When using fine quartz as an abrasive material, FRP showed higher mass losses in the aqueous environment than in the acidic conditions, especially at higher temperatures. In this case, the FRP degradation was governed by the penetration of the used medium into the FRP structure. According to the absorption studies, the weight gain of the laminate was more pronounced in the water immersion compared to the acidic solution, which can be a prediction of an increased degradation rate and explain the higher wear in the aqueous medium. When the abrasive material was changed from fine to coarse quartz, the removal of the shielding matrix phase was extensive and a direct route for the acidic solution to the fibres was created causing more severe damage. This was also shown in scanning electron microscopy (SEM) studies, where the samples tested in the acidic solution showed extensive fibre flattening along the erosion flux. By increasing the test temperature close to the boiling point of the medium, an increase in the FRP wear could be seen. The increase in the rotation speed, on the other hand, did not automatically mean higher mass losses. This shows that the wear environment in the present test device is highly complicated with several interrelated parameters affecting the results.

Keywords: Slurry erosion; Erosion-corrosion; Polymer-matrix composite; Erosion testing

Corresponding author: Reija Suihkonen (reija.suihkonen@tut.fi)

1. Introduction

Glass fibre reinforced polymers (FRP) are commonly used construction materials in challenging environments, such as chemical plants or industrial hydrometallurgical processes. The processing conditions in mineral leaching, for example, can be aggressive: the construction materials are exposed to sulfuric acid solutions (generally 0.5-15% H₂SO₄) that contain various ions, such as chloride, at elevated temperatures (up to 95°C) [1]. The materials are subjected not only to corrosive fluid but also to solid-particle erosion: an effective mixing of constituents, including hard mineral particles with varying chemical composition, hardness, and shape is required to ensure high process performance. In industrial use, the impeller blades in the hydrometallurgical reactors are subjected to highly erosive conditions and turbulent flow, which depend on the geometry of the used system [2-4]. The particle flow inside the reactor may be highly complicated and, therefore, the erosion performance of a material in a real industrial application may differ considerably from the performance observed in a certain laboratory-scale test system. **Consequently, a test apparatus, which mimics the actual industrial application as closely as possible, should be designed to address this problem.**

The performance of the FRP materials has been widely studied in aqueous [5-9] and acidic [10-13] environments, but hardly any studies combine erosion wear measurements in corrosive environment at elevated temperatures. It is well established that a prolonged exposure in water or in the acidic medium can damage the FRP structure, either in the fibre, resin, or in the matrix-fibre interface. Water, for example, can cause both reversible and irreversible changes in the resin, including hydrolysis, plasticisation, swelling, and

1 microcracking. Reversible changes can be recovered by drying but irreversible changes will alter the mechanical
2 properties permanently [8]. Moisture can also travel along the fibre-matrix interface, which can lead to
3 detrimental effects in the fibre-matrix bond and, therefore, in the mechanical properties of the composite [14,
4 15]. The diffusion rate is direction dependent: the rate is higher parallel to the fibres than normal to them [16].
5 Moisture diffusion is also faster in a composite that has exhibited mechanical damage [17]. Similarly, the
6 moisture uptake level and the chemical processes that lead to the degradation of the composite are more
7 pronounced as the temperature is raised [14]. The uptake of moisture diffusion is generally measured by weight
8 gain and Fick's law is generally accepted model for predicting the water absorption behaviour of composites.
9 However, non-Fickian behaviour can be observed in many cases due to the complicity of the absorption
10 behaviour [18]. FRP materials may exhibit, for example, uniform material loss, localised pitting, fatigue,
11 erosion, and delamination due to the acidic environment [16] and these may occur also simultaneously. The
12 constituent responsible for the composite failures in the acidic environment is the glass fibres rather than the
13 resin, which generally operates as a shielding barrier for the fibres [13].

14
15 A slurry pot type device has been commonly used to evaluate the erosion wear performance of different
16 materials [19-24]. Generally, the tests have been conducted with varying speeds, impingement angles, particle
17 sizes and shapes and it has given valuable information to be used e.g. in the material selection. Joshi *et al.* [22]
18 have, for example, used a self-made slurry erosion pot to evaluate the erosion performance of Al₂O₃ filled
19 glass/epoxy composite with varying impact angles, rotation speeds, and slurry concentrations. The results
20 showed that the slurry concentration has the most significant effect on the wear rates while the test speed
21 showed less impact on the results. It should be noted that in this type of tester, a precise control of the slurry
22 velocity and the particle impingement angle is challenging due to the complexity of the flow in the pot and,
23 therefore, the flow fields should be examined with the aid of computational fluid dynamics (CFD) modelling. In
24 this study, used erosion test apparatus was constructed to resemble an industrial leaching reactor as closely as
25 possible. During the design, CFD model was used to estimate the flow patterns inside the reactor. However, in
26 this study, the viewpoint was fully empirical and the main goal was to examine the erosion wear of FRP in
27 precise conditions set by the industrial application, where the mixing efficiency of the constituents is a key
28 factor for a successful and a cost-effective process. The study is a continuation of the research performed by
29 Sarlin *et al.* [25] on the slurry erosion wear of vinylester matrix composites in water medium with varying
30 rotation speeds, abrasive size, and slurry temperatures. These tests were conducted mainly with the coarse
31 quartz. It was noted that the highly complex wear conditions with several interrelated parameters caused some
32 unexpected erosion mass losses. The dominating wear mechanism was abrasive wear, although at low rotation
33 speeds the wear mode was rather fatigue-like. At high rotation speeds the cavitation erosion mechanism became
34 more dominant. The FRP structure was found to be prone to both erosive turbulent flow and cavitation. Unlike
35 metals, FRP was also sensitive to the abrasive concentration of the slurry and even low-energy particles caused
36 wear [25]. In this paper, the tests in aqueous environment were continued with fine quartz and the results were
37 compared to those obtained using sulfuric acid solution as the slurry medium.

38 2. Experimental details

39 2.1 Materials and sample characterisation

40 Since the goal of this study was to mimic the actual wear environment, the raw materials in the tested FRP
41 laminates were also chosen based on the materials that are used in the FRP structures in the industrial mineral
42 leaching processes. The tested vinylester laminate was manufactured by hand lay-up using epoxy vinylester
43 resin (Derakane Momentum 411-350 supplied by Ashland). Vinylester has good durability in acidic conditions,
44 since it has hydrolysable ester groups only at the ends of the polymer chains [5]. It also has more compact
45 network structure than e.g. polyester showing hydrolytic degradation rather in the sample surface than inside the
46 polymer bulk [26]. The manufactured laminate contained six layers of chopped C-glass strand mat with a
47 nominal weight of 300 g/m² and one layer of C-glass mat (30 g/m²) on both laminate surfaces (glass fibre
48 diameter ca. 16 µm). The structure of the laminate is similar to the corrosion-resistant layer typically used in the
49 surfaces of FRP structures employed in the leaching reactors. The goal of this C-glass barrier layer is to isolate
50 the load bearing structural layer from the process fluid. The laminates were post-cured for 4 h at 80°C. The
51 density was measured with a Wallace electronic densimeter, glass transition temperature (T_g) with a differential
52 scanning calorimeter (DSC, model Netzsch DSC 204) under a nitrogen flow (50 ml/min) at a temperature range
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1 of 25–200°C according to standard ISO 11357-1:2009. The fibre fraction of the laminates was measured with a
2 residual ash determination test, where a small sample (weight of approximately 1 g) was cut from the laminate
3 and its temperature was raised gradually to 600°C in an oven. After all the resin had burned away, the remaining
4 ash was weighed and compared to the original weight.

5 The erosion test samples (size 35 mm x 35 mm) were water jet cut from the laminate and the cut edges of the
6 samples were sealed with vinylester resin (Derakane 441 supplied by Ashland) in order to avoid excess water
7 intake. Vinyl ester resin was chosen as a sealant material to minimise the parameters affecting the results. To
8 reach a fixed reference state, the samples were placed in an oven (6 h at 80°C) and then weighed. After the test,
9 the worn samples were cleaned with a soft cloth and an ultrasonic cleaner in a water bath (1 h) to remove any
10 abrasive material attached to the sample surfaces and to minimise the amount of loose wear debris that would
11 affect the weight loss measurements. Finally, the samples were dried in an oven (6 h at 80°C), weighed, and the
12 mass loss values for each sample were calculated. The wear surfaces were characterised with a scanning
13 electron microscope (SEM, model Zeiss ULTRApplus) using an acceleration voltage of 10 kV. Prior to the SEM
14 studies, the specimens were coated with a thin gold layer to avoid charging. The surfaces of the selected
15 specimens were also characterised with an optical 3D measurement apparatus (Alicona InfiniteFocus G5).

18 2.2 Slurry erosion wear test set-up

19 Erosion wear tests were done with an in-house constructed erosion test apparatus (Fig. 1) that resembles the
20 reactors that are used in real-life mineral leaching processes. The slurry erosion test apparatus has been designed
21 with the help of CFD modelling to match the real-life leaching reactor as closely as possible in order to get
22 reliable and comparable test results and it has been previously described in detail [25, 27]. The sample holder in
23 this test apparatus resembles a typical agitator type that is used in mixing solids in leaching processes. Twelve
24 samples were attached to the agitator blades fixed at 45° position: half of them to the pressure side and another
25 half on the suction side. The CFD model demonstrated that the wear pattern on the pressure side is more or less
26 uniform, while a large trailing vortex is generated behind a moving impeller blade causing turbulence, which
27 can lead to extensive localised wear. This behaviour has been widely verified in the literature [28-31]. The test
28 construction allows a simultaneous study of two different wear phenomena, which, adding to the possibility to
29 change the tip speed, slurry temperature, and slurry properties (type of abrasive and used liquid as well as slurry
30 concentration), make this type of apparatus a valuable tool for optimising the service life of materials in real-life
31 processes.
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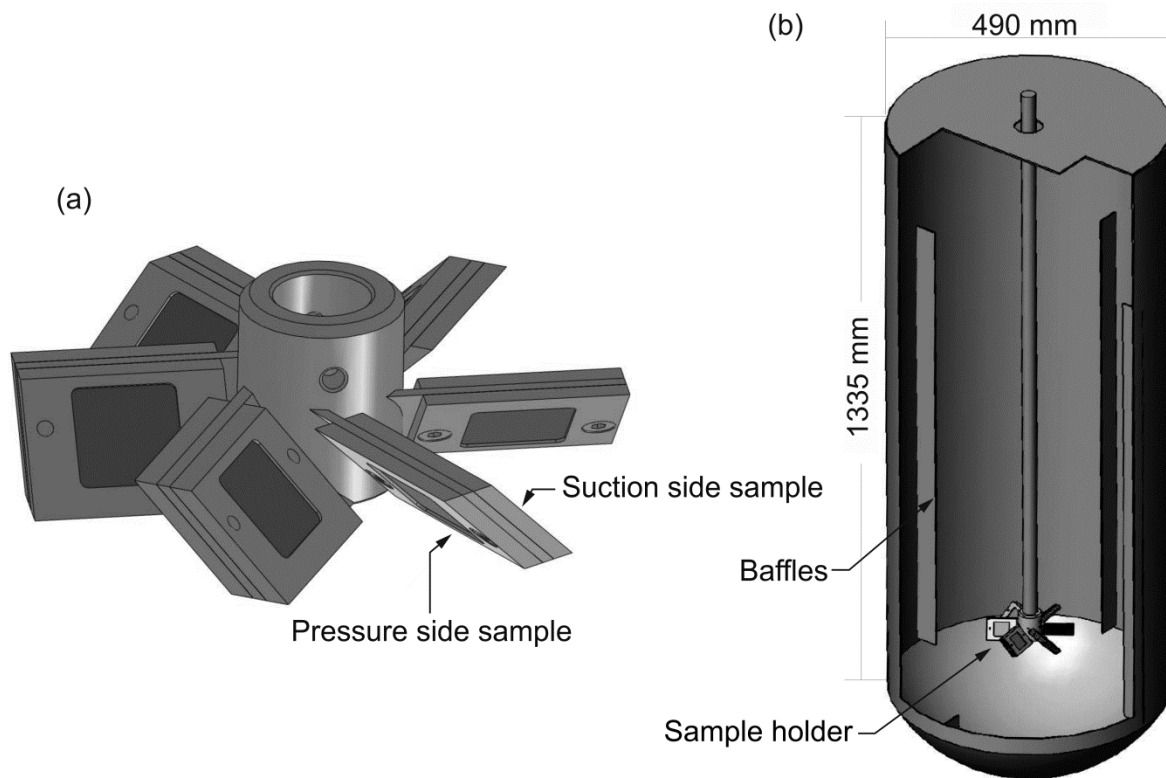


Figure 1: Schematic image of (a) the impeller to which the samples were attached and (b) the testing apparatus with the impeller (modified from [H19])

In this study, slurry erosion wear of FRP materials was studied in two different environments: water and 5% sulfuric acid (H_2SO_4 , concentration measured in wt.%) solution. H_2SO_4 solution contained ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$, 0.5 g/l), which is often present in leaching environments. In this study, the role of ferric sulphate was to act as a corrosion inhibitor for the stainless steel parts of the device. The viscosities of pure water and the acidic solution, measured by the Anton Paar AMVn Automated micro viscometer, showed no difference either in 20°C or in 90°C. In 95°C, the measurement was not possible with this equipment due to the air bubbles created in the liquid.

Before the tests, the tank was filled with 180 litres of liquid and 30 kgs of abrasive material. This corresponds roughly the abrasive concentration of 15 wt.%, which is typical for many hydrometallurgical processes. According to settlement studies, both quartz abrasives behaved in a similar way forming most of the sediment layer as the mixing was stopped. Coarse quartz may fall faster into the bottom of the container, while the finest particles in fine quartz may drift slightly longer along the liquid medium. Due to the relatively low abrasive concentration in the slurry and the tendency of the particles to fall into the bottom of the container, the slurry viscosities could not be measured reliably with the apparatuses available. The formation of the sediment layer was, however, similar in aqueous and in acidic slurries. In the erosion tests, four baffles inside the reactor prevented the flocculation of the abrasive materials and no heavy sediment layer was formed in the bottom or in the walls and, therefore, it was assumed that all used slurries were homogenous during the test. Two quartz abrasives (Nilsjö quartz supplied by Sibelco Nordic Oy Ab) with different particle sizes were used and their properties are summarised in Table 1. The detailed analyses of the abrasive materials are reported elsewhere [25, 27]. The quartz abrasives were considered to be chemically inert even though some impurities, visual to eye, could be observed especially in coarse quartz. The mass loss of the quartz abrasive during 72 hours of exposure in the acidic solution at 95°C was negligible (< 1 wt.%) and was thought to originate from their grinding to finer particles, which went through the used filters along with the liquid, rather than their dissolution in the acidic solution.

Table 1: Properties of the quartz abrasives [25, 27]

Abrasive	Density (g/cm ³)	Nominal particle size (µm)	D50 (µm)	D80 (µm)
Fine quartz	2.66	50–200	120	150
Coarse quartz	2.70	100–600	280	400

The test parameters were chosen based on the actual parameters that are used in industrial mineral leaching processes. The acidic solution in these processes varies between 0.5-15%, and acidic content on the low side (5%) was chosen due to the safety issues. The 5% acidic solution is generally combined with high temperature (95°C). Tip speed was also chosen based on the rotational speeds used in the actual impellers in the production scale equipment (generally > 4.5 m/s) and the upper limit set by the slurry erosion test apparatus itself (7.2 m/s). Test time (72 h) was chosen so that during that time, a reasonable wear could be achieved to the samples and the tests in the acidic environment could be done safely during one working week. In the beginning of the test, the slurry was heated either to 80°C or 95°C using two heating coils situated at the lower section of the reactor. The temperature during the test was monitored continuously with thermocouples. The rotation speed used was 4.8 or 7.2 m/s. Some safety precautions needed to be implemented when handling large amounts of hot acidic solution. As a comparison to the tests in the aqueous environment, where every test was conducted with fresh abrasive sand, a small amount of sand was left inside the reactor together with the acidic solution after each test. The amount of the removed abrasive sand was measured and it was replaced with fresh sand. The reactor was fully emptied after five consecutive runs. Furthermore, after each test, the acidic solution was allowed to cool down to room temperature before removing the samples from the reactor. Since the tests were carried out close to the boiling point of the liquid medium, a solution sample was taken after each test and its acid concentration was measured with an iodometric titration to maintain similar solution properties throughout the test series. The test environment, quartz abrasive material, test velocity, and slurry temperature were altered according to Table 2 in order to study the effects of these parameters on the erosion wear of FRP both in aqueous and acidic environments. In this study, two to six samples were generally tested in each condition.

Table 2: Test matrix

Test environment	Quartz abrasive	Slurry concentration (wt.%)	Tip speed (m/s)	Nominal slurry temperature (°C)	Test duration (h)
Water	Fine	15	4.8	80	72
5% H ₂ SO ₄	Fine	15	4.8	80	72
Water	Fine	15	4.8	95	72
5% H ₂ SO ₄	Fine	15	4.8	95	72
Water	Coarse	15	4.8	95	72
5% H ₂ SO ₄	Coarse	15	4.8	95	72
Water	Fine	15	7.2	95	72
5% H ₂ SO ₄	Fine	15	7.2	95	72

3. Results

The erosion wear of the samples followed a well-known [3, 25, 27, 28] behaviour: a rather uniform wear in the pressure side and a localised wear caused by the trailing vortex in the suction side could be seen (Fig. 2). In the suction side, the trailing vortex created a massive crater in the upper corner of the blade, close to the axis. The samples in the suction side showed also several grooves and pits, which were mainly concentrated on the surroundings of the large cavitation pit. On the pressure side, wear was more uniform, but a small crater created by the localised wear was located in the inner corner of the blade. The location of the cavitation pit was the same in all the pressure side samples tested with the fine quartz. In the case of coarse quartz, it has been previously noted that the combination of higher rotation speed and the coarse abrasive material created the pit in the other side of the sample, outer corner, where the tip speed was as its highest [25]. This behaviour was

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verified in this study when the abrasive material was first changed from fine to coarse quartz: at lower rotation speed (4.8 m/s), small cavitation pits were generated on the both edges of the samples. As the test speed was increased, the size of the inner edge cavitation pit was decreased. At the tip speed of 7.2 m/s, the creation of the cavitation pit in the outer edge of the blade was fully dominating over the formation of the inner one. Apparently, the increase in the rotation speed combined with the higher abrasive particle size changed the slurry flow patterns inside the reactor. These changes may originate from the increased interactions and collisions of the larger particles with each other and with the gas bubbles created in the slurry at 95°C.

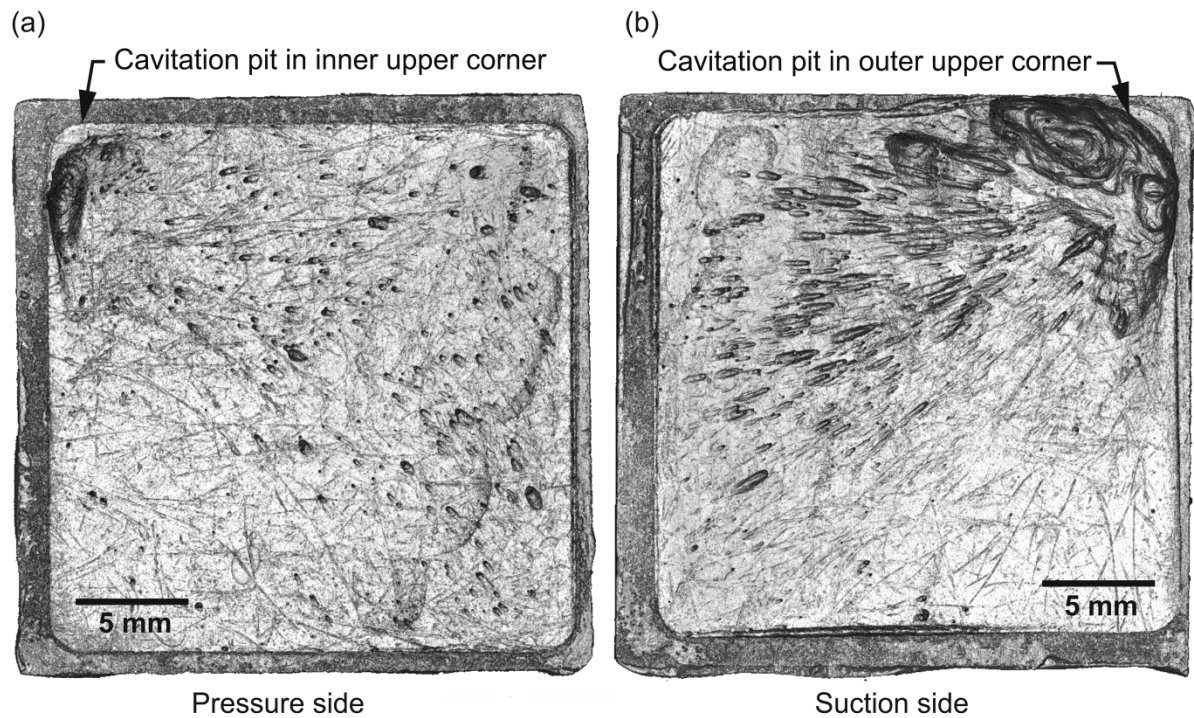


Figure 2: The surfaces of the typical (a) pressure and (b) suction side samples tested with the fine quartz

3.1 The effect of test temperature

Both in the aqueous and acidic mediums, temperature increase accelerated the wear of FRP (Fig. 3). This was expected due to the softening of the matrix at higher temperatures. In addition, all samples tested at 95°C were whiter in their colour than the samples tested at 80°C, probably due to the hydrolytic degradation of the matrix material at higher temperatures [25, 26]. All the samples exhibited some fading in the surface colour after the test, but the colour difference was more pronounced with the samples tested in the aqueous environment i.e. they were whiter than the ones tested in the acidic solution. An increase in the test temperature has shown to increase the water permeation rate of the laminate, which, on the other hand, can be a prediction of decreased mechanical properties [12]. At the test temperature of 80°C in the acidic environment, the samples obtained similar or even slightly higher wear rates than the ones tested in the aqueous conditions, showing opposite behaviour compared to the results at 95°C. As the test temperature is close to the boiling point of the liquid medium, a gas phase is introduced to the system, which leads to increased cavitation erosion. Cavitation erosion is typical in propellers and turbine blades operating in wet stream and its characteristic feature is the collapse of the formed gas bubbles near the solid sample surface. When a bubble collapses, surrounding liquid rushes to fill the created void and collides with the surface creating large stresses to the solid and round craters on the surface. Cavitation can be further accelerated by the hard particles present in the slurry medium since they hit the surface with high velocity [32]. Since the acidic solution has slightly higher boiling point (measured value 102,9°C) than water, the amount of gas bubbles may be higher in the water medium than in the acidic solution when the test temperature is 95°C. The increased amount of gas bubbles cause more collisions in the sample surface, which, on the other hand, lead to higher stresses and increased material removal. Accordingly, SEM images

(Fig. 4) show large cavitation pits in the sample tested at 95°C, while the corresponding sample tested at 80°C shows clearly smoother surface.

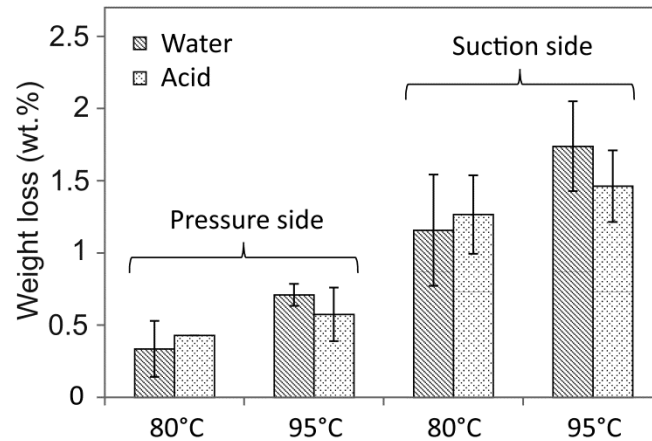


Figure 3: The effect of temperature on the FRP wear (4.8 m/s, fine quartz, 72h). The error bars describe the standard deviation of the results.

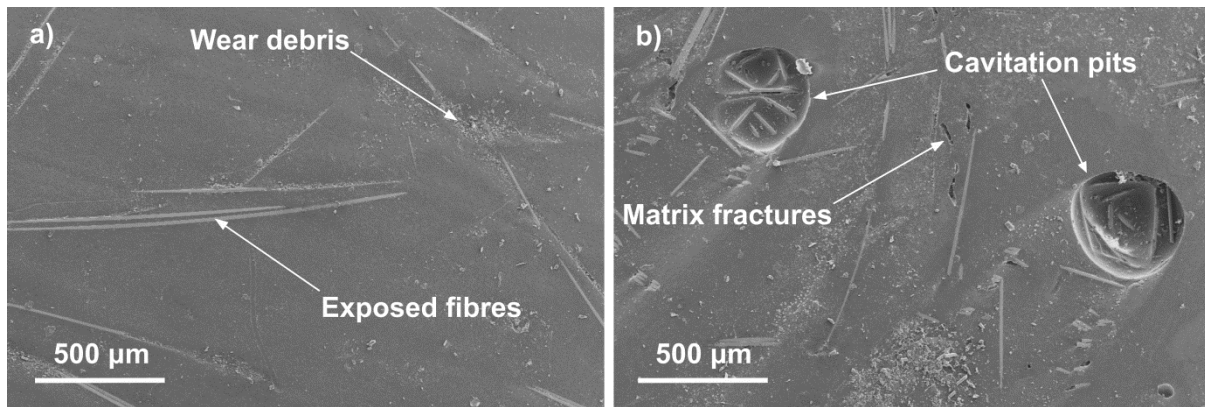


Figure 4: SEM images of the sample surfaces tested at (a) 80°C and (b) 95°C in acidic environment (suction side, fine quartz, 4.8 m/s, 72h)

DSC studies (Table 3) on the samples tested in water and in the acidic solution were conducted to estimate if any polymer degradation had occurred during the erosion test. In comparison, few samples were also heat-treated in an oven for 72 hours at 80°C or 95°C. The previous results showed that the samples were not fully cured during the manufacturing of the laminate [25]. That means that there are unreacted monomers in the structure when the samples were exposed to erosive wear in the aqueous or acidic medium. Some curing in the manufactured laminate occurred when the vinyl ester, used to seal the open edges of the laminates, was cured in the oven prior testing. Final curing took place during the erosion test, since no exothermic peak was noticed in the DSC curves of the samples that had experienced the three-day erosion test. However, according to the DSC results, T_g values did not markedly drop, which indicates that there was no significant deterioration in the matrix material. However, the elevated temperatures induce the crosslinking of the unreacted monomers, which generally can be seen as an increase in the curing degree and the T_g value of the material. Some researchers have also noted an increase in the T_g value after a water immersion test and concluded that it is originated from the leaching of monomers and an anti-plastisation effect in the structure [5]. It is thus possible that several phenomena, crosslinking, hydrolysis, and leaching of monomers, occurred in the matrix when subjected to the aqueous and acidic mediums at elevated temperature, which counterbalance each other. The final outcome then depended on the relative strengths of the competing mechanisms.

Table 3: Averaged T_g and standard deviation values of the oven-treated and the erosion tested samples in the aqueous and acidic mediums

Temperature (°C)	Medium	T_g (°C)
80	Air	106.7 ± 0.6
	Water	104.9 ± 0.2
	5% H_2SO_4	105.6 ± 0.8
95	Air	107.9 ± 0.6
	Water	107.5 ± 0.8
	5% H_2SO_4	108.4 ± 0.8

3.2 The effect of particle size

Quartz particles are irregular in shape and have sharp edges, which can cause cutting and brittle fragmentation to the sample under erosion. It has been previously demonstrated by the SEM analysis and SPQ (spike parameter – quadratic fit) parameter measurements that the fine and coarse quartz abrasives had no differences in shape [27]. Theoretically, as the kinetic energy of the abrasive particles is increased, the damage upon impingement is increased. Factors that influence the kinetic energies (E_k) and, therefore, the erosivity of the particles are the density, velocity, and size of the abrasive particles according to the equation $E_k = 2/3\rho\pi R^3V_P^2$ [33], where ρ is density, R particle radius, and V_P velocity of the particles. As the densities of the both quartz particles are practically the same, the differences in the kinetic energies originate from the differences in their particle sizes. Therefore, the wear rate caused by the coarse quartz should be markedly higher than for the fine quartz. This behaviour is clearly evident in our studies in the acidic environment. Figure 5 shows that the mass loss of the pressure side samples tested with the coarse quartz was over twice as high as tested with the fine quartz. In the suction side, with the trailing vortex dominating the wear process, the increase was not that drastic, but still clear (+36%). In the water medium, this observation was valid only in the pressure side. In the suction side, the mass loss was decreased as the particle size was increased. This behaviour was explained in our previous study as the lower viscosity of the slurry containing abrasive with the higher particle size [27]. This, however, does not apply to the acidic medium and thus proves that one cannot separate one factor from the very complicated wear environment. The factors that influence the outcome, especially at temperatures near the boiling point of the liquid, are the presence of the gas phase, the size and the amount of the gas bubbles in the liquid, as well as the collisions between the particles, sample surface, and the gas bubbles. Their joint effect varies as the test parameters are changed and even a subtle change in the parameters may substantially change the flow patterns inside the reactor. For example, the collisions between the particles and the gas bubbles are more probable with the abrasive with higher particle size and, therefore, the kinetic energies of the coarse quartz may not be as high as it is theoretically estimated. As the amount of the gas bubbles is higher in the aqueous medium, e.g. due to the slight difference in the boiling points of the used mediums, their effect in decreasing the kinetic energies of the coarse quartz particles may also be more significant than in the acidic medium.

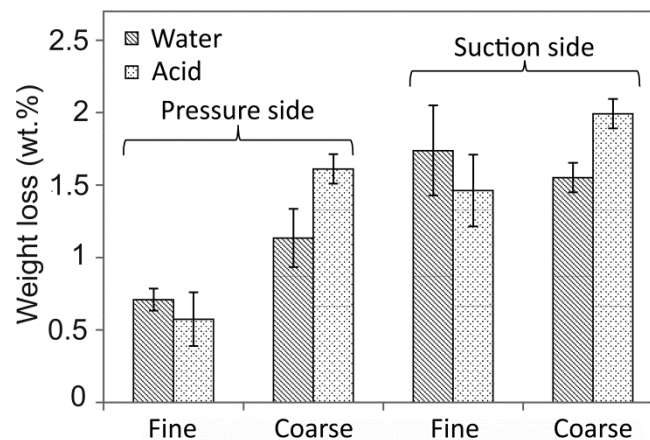


Figure 5: The effect of abrasive particle size on the FRP wear (4.8 m/s, 95°C, 72h). The error bars describe the standard deviation of the results.

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As a contrary to the fine quartz, the coarse quartz caused higher wear in the acidic medium than in the aqueous environment. This was because the coarse quartz, with the particles having higher kinetic energies, was able to break the shielding resin layer more rapidly than the fine quartz. After the route to the fibres was established, corrosive medium was more harmful to the fibres than water. With the fine quartz, the erosion wear was mainly governed by the hydrolysis and the penetration of the liquid through the laminate and the role of the mechanical damage caused by the abrasive particles was smaller. This behaviour can be clearly seen in Figure 6, where the coarse quartz has caused severe material removal, mainly through the round pits crated by the cavitation erosion, from the FRP surface compared to the fine quartz.

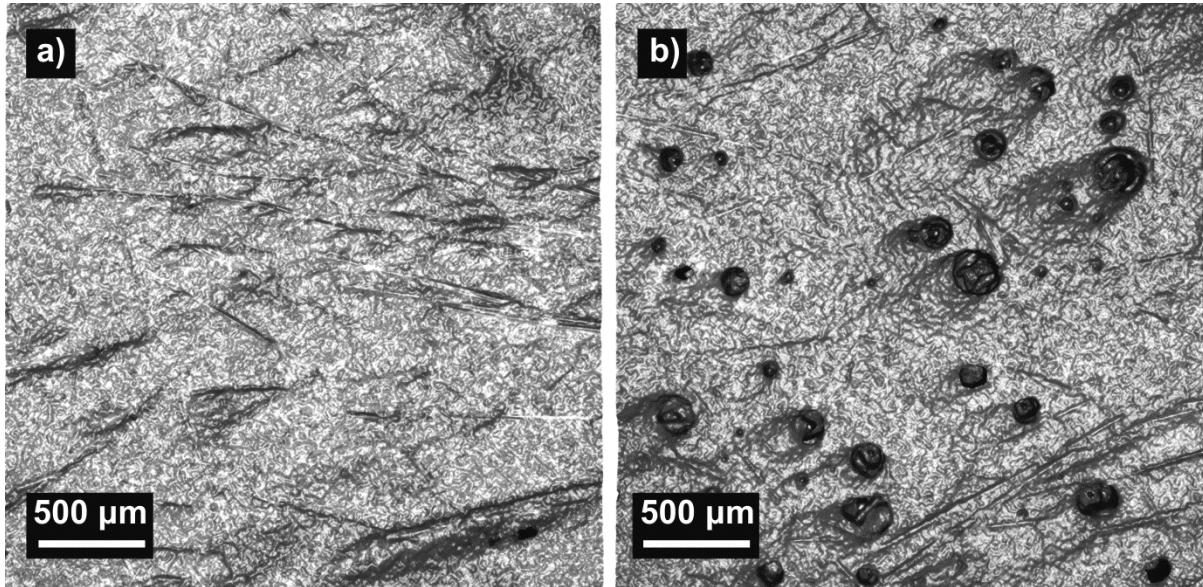


Figure 6: Examples of the FRP surfaces tested with a) fine and b) coarse quartz abrasives in acidic medium. Surface profilometer images have been taken from the same position in both samples, in the middle of the suction side sample

3.3 The effect of tip speed

The increase in the tip speed increased the wear in the pressure side, while on the suction side, an opposite behaviour was noticed (Fig. 7). This observation applied in both water and acidic mediums and it has also been verified in our earlier papers [25, 27]. Theoretically, increasing the tip speed should also increase the wear. Drensky [34], for example, has made such observations with the carbon fibre reinforced composites: higher wear rates were obtained when the test velocities were increased. In this study, this theory applies to the pressure side, where the wear is more uniform and the samples exhibit similar wear rates in the aqueous and acidic conditions. However, when inspecting the suction side results, the FRP wear decreased when the tip speed was increased. In this case, the presence of the trailing vortex has to be taken into consideration. As the tip speed was increased, the sample could also escape the trailing vortex more rapidly. In addition, the presence of the gas phase at the test temperature of 95°C promotes cavitation wear but at the same time, the collisions between the gas bubbles and the abrasive particles may reduce their kinetic energies causing lower wear rates than expected. Therefore, the evaluation on the effect of the tip speed is not that straightforward. At a certain combination of parameters, another factor may dominate over another causing new flow patterns inside the test reactor and unexpected mass losses for the samples.

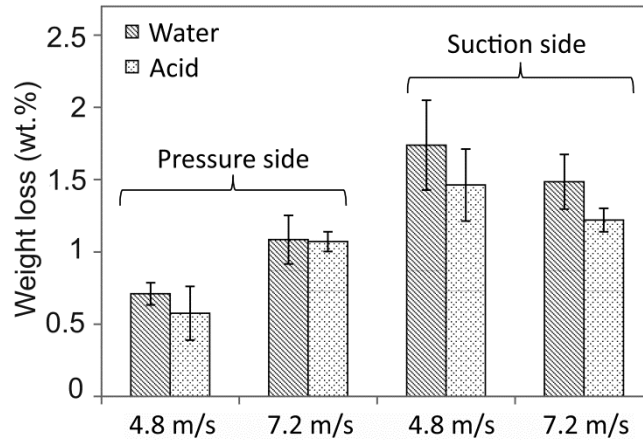


Figure 7: The effect of the tip speed on the FRP wear (95°C, fine quartz, 72h). The error bars describe the standard deviation of the results.

3.4 The effect of the FRP properties

To study the effect of the laminate properties on the erosion wear, a comparison sample for Derakane 411-350 based laminate (411) was manufactured using Derakane 441-400 epoxy vinyl ester resin as a matrix material (441). 441 resin has better thermal properties than 411, which is seen as higher heat distortion temperature (HDT) (120°C for 441 [35] and 105°C for 411 [36]) and T_g value (125°C for 441 [35] and 120°C for 411 [36]).

The erosion test results for the samples (Fig. 8) show that the sample with the 441 resin showed better erosion wear properties both in the aqueous and in the acidic conditions than the sample with the 411 resin. The main reasons behind this are the better thermal properties and the substantially lower fibre content of the 441 laminate (Table 4). It is generally accepted that the increase in the fibre content deteriorates the erosion properties of FRP [37]. On the other hand, the test temperature is so close to the HDT of 411 that it starts to soften during the test, which can increase the material removal.

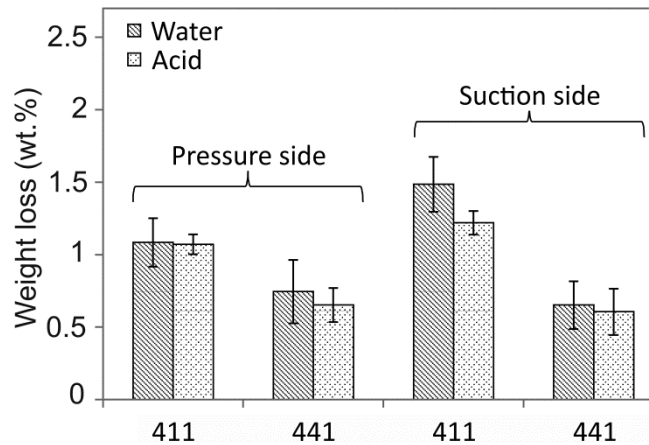


Figure 8: Slurry erosion mass losses of FRP laminates with Derakane 411 and Derakane 441 as the matrix material (95°C, 7.2 m/s, fine quartz). The error bars describe the standard deviation of the results.

Table 4: Properties of the tested FRP laminates

Resin used in the laminate	Density (g/cm ³)	T_g (°C)	Fibre content (wt.%)
Derakane 411-350	1.42	117	40
Derakane 441-400	1.32	120	22

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When inspecting the worn samples, it can be seen that the erosion damage was clearly more severe in the 411 samples than in the 441 samples (Fig.9). The large cavitation pit in the suction side caused by the trailing vortex was deeper in the 411 sample than in the 441 sample and it was surrounded by several macro-sized grooves and pits. Some wearing had occurred also in the other parts of the sample while the 441 sample showed very smooth surface outside the localised wear pit created by the trailing vortex. Even though it was assumed that the edges of the samples were not subjected to erosive wear, the sample holder created some pressure to the sample edges during the attachment of the sample, which, together with the elevated temperature, created some irreversible deformation on the surface.

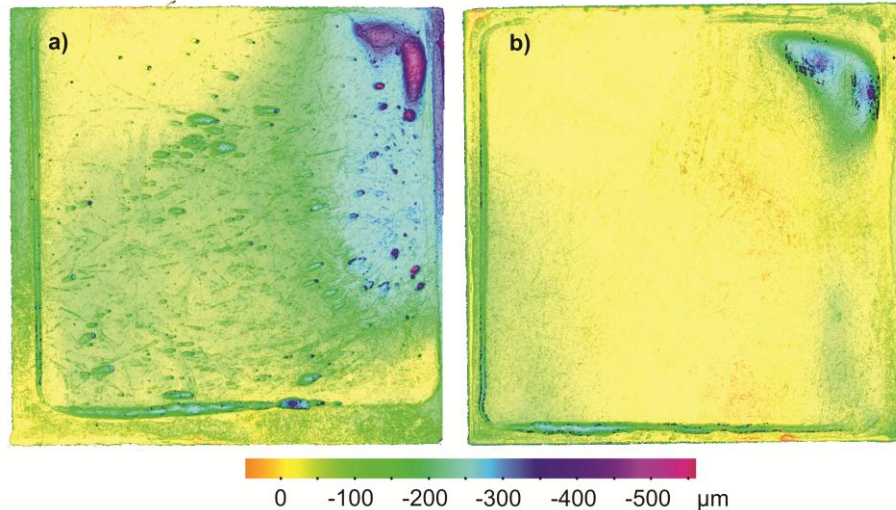


Figure 9: The surface topographies of (a) 411 and (b) 441 based FRP samples (suction side, acidic medium, 95°C, 7.2 m/s, fine quartz)

The SEM images (Fig. 10) showed that the surface of the 441 sample was smooth with only narrow grooves. What was more distinct, it showed hardly any micro-sized cavitation pits that were covering the whole 411 sample surface after the erosion test at 95°C. Thus, the 441 FRP sample tolerated the cavitation erosion well and it was not that prone to the formation of microfractures that can lead to massive matrix removal during the erosion test. Both samples behaved similarly in the aqueous and acidic conditions showing lower wear rates in the corrosive environment. However, the wear rates of 441 were the same in the pressure side than in the suction side even though it is generally accepted that the trailing vortex behind the impeller blade leads to higher mass losses. The results show that by carefully designing the raw materials and the structure of the manufactured FRP laminate, clear improvements in the erosion properties can be achieved.

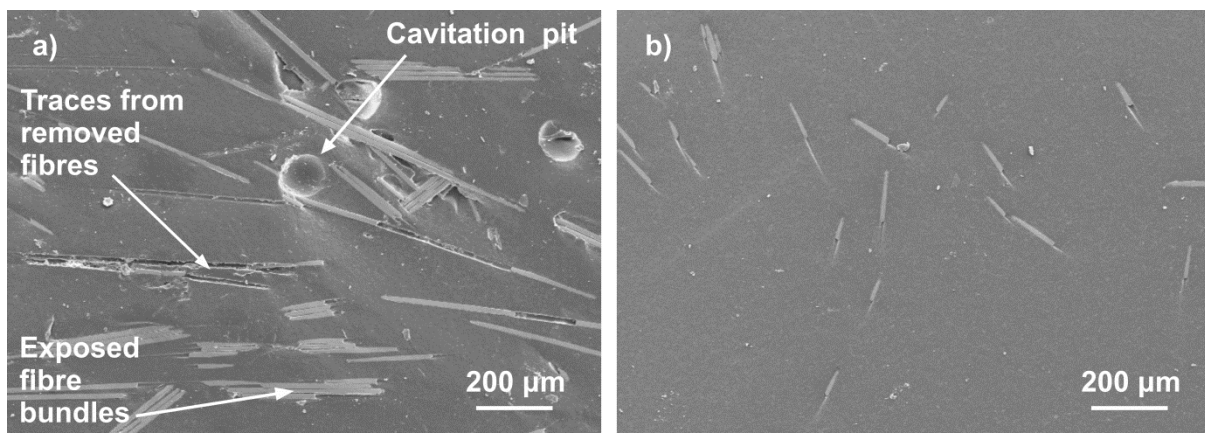


Figure 10: SEM images of the surfaces of the FRP samples based on a) 411 and b) 441 matrix after the erosion test in acidic solution

4. Discussion

The obtained test results show that the erosion wear properties of FRP are strongly affected by the test parameters and the wear environment present in the used test reactor. However, the weight loss results need to be correlated with the SEM analysis on the worn sample surfaces to fully understand the wear mechanisms in the FRP structure. The degradation of FRP structure in aqueous medium is associated with the hydrolysis of the matrix and the fibre and the destabilisation of the matrix-fibre interface. Small water molecule penetrates easily into the polymeric network and, in addition to hydrolytic reactions, it can degrade the material also by the leaching of small molecules (monomers or oligomers) [26]. Hydrolysis can induce ion exchange reactions in glass fibres, which can lead to flaw initiation and propagation when load, such as hydrostatic pressure in tanks, is applied. Water also promotes the production of free alkali hydroxide groups that can accelerate the degradation of the silica structure of the fibre and further catalyse the hydrolysis of the ester groups of the resin [5, 15]. The wear of FRP in the corrosive medium followed broadly the same route as in the aqueous medium reported earlier [25]: SEM analysis showed that there were imprints of abrasive wear in the surface, which is typical for low angle collisions [32]. Samples exhibited brittle erosion behaviour, where microcracks were formed into the matrix material leading eventually to its removal from the surface (Fig. 11a). In corrosive environment, this was a conclusive step since the resin acts as a shielding barrier for the fibres. If the resin barrier layer is damaged in any way and the acidic solution reaches the brittle fibres, degradation becomes rapid and may cause catastrophic failure. As the abrasive particles created massive localised wear pits to the sample surface, the fibre surfaces were exposed to the combination of erosive particles and corrosive fluid. The generally accepted mechanism of the corrosion process of the glass fibres is an ion exchange reaction, where the metal ions in glass surface are replaced by the H^+ from the acidic medium [13]. The leaching of network modifiers such as Ca^{2+} , Al^{3+} , Fe^{3+} , Na^+ , and other residuals can lead to e.g. pitting [38] so that eventually, a weakened sheaf is created. Leaching in corrosive medium can also lead to spiral cracking even if the fibres are not under stress during the immersion. These cracks form when the corrosive environment is removed and the hydrated sheaf dries out [39].

What was noticeable in the samples tested in the acidic medium was that the appearance of the exposed fibres was flattened (Fig. 11b), hardly any round fibres were found on the surface. It is evident in the SEM images that the glass fibres started to erode along the slurry flow as soon as they were exposed to the acidic solution. In our previous study in the aqueous medium, the amount of these fibres was not significant until the temperature reached 95°C or at the high rotation speeds and it was thought to originate from the brittle fraction of fibres created by the collapsing vapour cavities [25]. Here, using the fine quartz abrasive in the aqueous medium, some round fibres could be found at lower rotation speeds in areas that were not subjected to extensive localised wear. In the acidic environment, the fibre flattening was visible already at lower tip speeds and temperatures, and the damaged fibres were located all over the sample, not only in the areas of highest wear. The flattened fibre surfaces were smooth and, generally, no massive cracks were found in the longitudinal or transverse direction. Being in a direct contact with the glass fibre surface, the acidic fluid is able to leach ions from the structure, making it weaker and more vulnerable to the multiple collisions caused by the abrasive particles and/or local pressures created by the vapour cavities bursting near the surface. Eventually, as the fibres got thin enough, even a small transverse fracture led to the breakage of the fibre to parts and their detachment from the matrix. In addition to notches and sharp dents, the matrix material showed distinct grooves that the glass fibres left behind after they were detached from the matrix. Marks of cavitation wear could be observed also in the acidic environment (Fig. 11c), and the amount of the cavitation pits was markedly higher when tested at 95°C compared to 80°C. The cavitation erosion can affect significantly to the formation of the large cavitation pit in the suction side. Together with the trailing vortex, localised pressures caused by the bursting vapour cavities can remove large amounts of material from the surface. This was evidenced by the images of the sample surfaces in Figures 2 and 9, where a large amount of smaller round pits was focused on the surroundings of the massive cavitation pit caused by the trailing vortex.

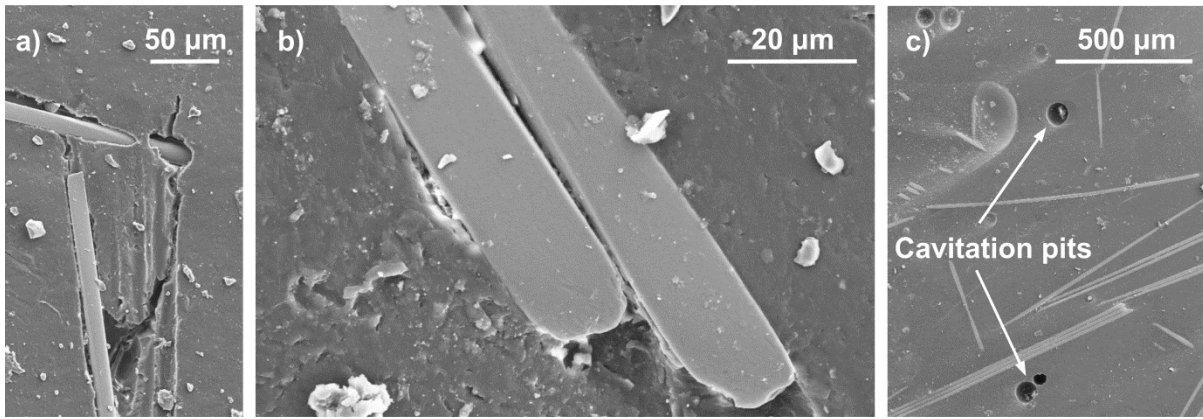


Figure 11: SEM images of the FRP sample surfaces after erosion test in acidic environment (a) matrix fractures, (b) flattened glass fibres, and (c) round cavitation pits in the matrix

At the test temperature of 95°C, both in the pressure and in suction sides, the wear of the samples was higher in the water medium than in the acidic conditions. In fact, water seemed to cause more severe damage to the material than the acidic solution when the abrasive material was fine quartz. The fine quartz was able to break the shielding resin barrier mechanically only to a certain level and, thus, the degradation was mainly governed by the water or acid penetration through the resin. In order to study this phenomenon, the FRP samples (size 35mm x 35mm x 3mm) were immersed in water and in the sulfuric acid solution at 95°C for 14 days. Before the test, the edges and the backside of the samples were sealed with the vinylester resin. The mass of the samples was measured after 1, 3, 6, 12, 24, 36, and 48 hours and after that once a day. Weight gain was calculated from five parallel samples. The results (Fig. 12) show that water penetrates into the FRP structure more rapidly than the sulfuric acid solution. In fact, after 72 hours, the weight gain of FRP in the water medium was 50% higher than the weight gain in the acidic medium. Water intake did not reach equilibrium during the 14-day test, while the FRP sample weight in the acidic solution remained constant or even started to decrease after two days of immersion. According to the supplier, the maximum service temperature for Derakane 411-350 is 100°C both in water and in 5% H₂SO₄ mediums [40] and, therefore, it was assumed that there was no significant deterioration in the matrix phase. C-glass, on the other hand, has showed a weight loss of 2.2 wt.% after exposing it to 10% H₂SO₄ solution for 24 hours [16], which could explain the small mass loss in the sulfuric acid solution. On the other hand, it has been concluded that the resin-rich layer, generally placed on the exposed surface, or in this case inside the hydrometallurgical reactor, cannot be considered as a barrier with respect to water, but it functions well in resisting the penetration of SO₄²⁻ ions. H⁺ and SO₄²⁻ ions travel through the laminate structure at a much slower rate than the water molecules and the water permeation rate through the laminate is decreased as the H₂SO₄ concentration is increased. In fact, according to the studies conducted by Regester *et al.*, acid has an ability to set up a barrier for diffusion, since the water permeation through the laminate showed a sharp drop after a few months immersion to sulfuric acid solution with varying concentrations while the water permeation rate for the 15% HCl and distilled water did not change over a 3-month period [12]. In this case, the weight gain of FRP in acidic solution can be regarded as a joint effect of the molecule penetration through the matrix and the possible degradation of the C-glass fibres.

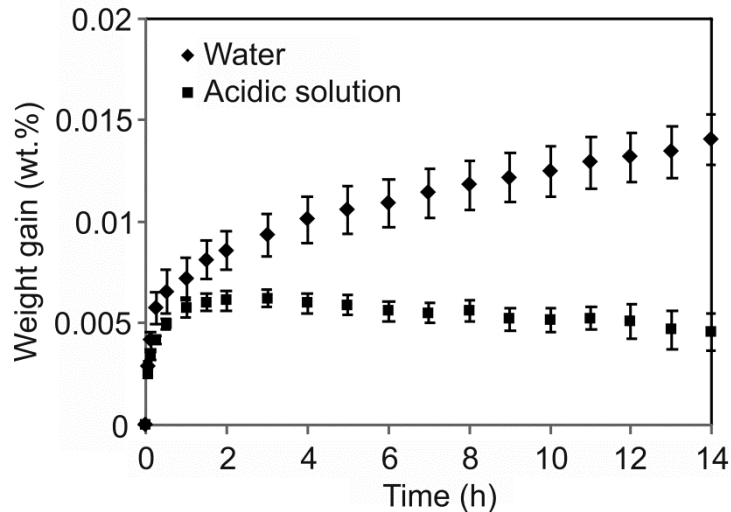


Figure 12: The weight gain of the FRP laminate sample during the immersion test in water and sulfuric acidic solution at 95°C. The error bars describe the standard deviation of the results.

5. Conclusions

This work demonstrated an in-house testing apparatus that mimics an actual wear environment in the mineral leaching process. Erosion tests were conducted in aqueous and acidic environments at elevated temperatures with various test parameters. To conclude the main test results, the following remarks can be done:

- At test temperature of 80°C, the acidic solution caused similar or even slightly higher wear rates than the aqueous medium when the abrasive material was fine quartz. An opposite result was obtained at 95°C, where water caused more severe damage to the material than the acidic solution. At 95°C, the gas phase was introduced to the system causing cavitation wear that increased the total wear rates. In addition, the softening of the matrix material occurred at higher temperatures, which increased the wear.
- With the fine quartz, the degradation was mainly governed by the penetration of the used medium through the resin, while coarse quartz was able to mechanically break the shielding barrier more rapidly. When the path to the glass fibres was opened, the sulfuric acid solution attacked the fibres and caused severe damage, such as extensive fibre flattening.
- The penetration of the small water molecules into the FRP structure was rapid and the weight gain was increased as a function of time. With the sulfuric acid solution, the weight gain remained constant or even started to decrease after two days of immersion.
- The increase in the tip speed strongly affected the flow fields in the slurry: the wear in the pressure side increased, while the opposite behaviour was noticed in the suction side. The increase in the tip speed, together with the gas phase present at 95°C, caused changes in the slurry flow resulting in unexpected mass losses for the samples.
- Laminate with the lower fibre content and Derakane 441-400 vinyl ester as the matrix material operated well in both conditions. As the sample with 411 resin showed clear surface erosion after the test, the sample with 441 exhibited smooth surface with hardly any scratches. It also had superior resistance to cavitation erosion compared to the sample with 411 resin since hardly any cavitation pits were observed in the sample surface.

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