

Article

Effects of Fuel Hydrochloric Acid Contamination on Selected Metals

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Abstract: Chlorinated organic compounds, as contaminants in marine fuels, have caused severe damage, affecting both main and auxiliary engines. Contaminated fuels can cause serious damage to an engine and its components, corroding fuel pumps and blocking filters, for example. This affects the operation of the engine, and, in the most severe cases, vessel safety. This study considered fossil diesel containing hydrochloric acid as a possible product formed under certain conditions in fuel contaminated with COCs and its effects on carbon steel, stainless steel, tempering steel, and aluminum. Five fuel samples with different concentrations of hydrochloric acid were prepared, plus one sample of diesel and water. Metal bars were partially immersed in the fuel samples and stored at room temperature for approximately one month. A visual assessment found corrosion across the entire surface of all metal bars when exposed to fuel samples containing hydrochloric acid. Even the smallest acid content (25 ppm) caused corrosion, and the effects were already observable after only two days of exposure. Despite their acid contamination, the measured fuel properties fulfilled the standard for automotive fuels at the beginning of the test. The water in the diesel sample did not cause any visible corrosion.

Keywords: diesel fuel; fuel contamination; chlorinated organic compounds; hydrochloric acid; corrosion of metals



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1. Introduction

Contaminated marine fuels can cause harm to vessels. There are several reported cases where the supplied fuel has damaged engines. A fuel contamination case in 2023 identified the contaminants as di-hydro dicyclopentadiene and tetra-hydro dicyclopentadiene, which caused operational issues and the failure of auxiliary engines [1]. There are also several suspected instances of chlorinated organic compounds (COCs) causing contamination to marine fuels [2]. In a verified incidence in Asia in 2022, about 200 ships were supplied with high-sulfur fuel oil (HSFO) that contained COCs, and more than 100 ships had reported issues with fuel pumps and engines [2,3]. Chlorinated hydrocarbons, as contaminants, have caused severe damage to both main and auxiliary engines and other problems, such as corrosion of the fuel pump and blocked filters [4]. The COC concentration in the 2022 incident was measured to be up to 21 000 ppm at one point in the delivery chain [5]. Contaminated fuels can cause serious damage to an engine and its components, which, in turn, affects the operation of the engine and, in the most severe cases, a vessel's safety.

Fuels should fulfill prescribed standards when supplied. Requirements for marine fuels are set in standard ISO 8217 [6]. Paragraph 5.2 in Clause 5 states that the fuel should not contain material that would be "harmful to personnel, jeopardizes the safety of the ship, or adversely affects the performance of the machinery" [6]. Clause 5 does not specify specific test methods, but the fuel oil supplier has to fulfill the entire ISO 8217 standard [2]. If it can be proved that the vessel suffered damage from the fuel supplied, it can be assumed that the fuel has not met the ISO 8217 standard [2].

In one case of marine fuel contamination caused by chlorinated hydrocarbons, the identified contaminant compounds were 1,2-dichloroethane, 1,1,2-trichloroethane, tetrachloroethylene, and chlorobenzene [4]. Most of these are manufactured chemicals [7], and thus, they do not occur naturally in the environment. Two of them, 1,2-dichloroethane and 1,1,2-trichloroethane, are used as solvents, and tetrachloroethylene and chlorobenzene are used in degreasing [7]. These compounds are not used in crude oil refining [4].

It is possible that organic chloride contaminants in the fuel form corrosive hydrochloric acid in an engine's fuel system. Bureau Veritas [8] claims that fuels containing chlorinated hydrocarbons need to be heated to 98 °C in the separators and to about 130 °C at the engine inlet because of their viscosities. In principle, this leads to the vaporization of 1,2-dichloroethane and tetrachloroethylene, which, according to Wu et al. [9], can result in the formation of hydrogen chloride gas. Wu et al. [9] used a computational method to study the possibility of low-boiling organic chlorides in gaseous form producing hydrogen chloride in a hydrolysis reaction. Among other compounds, they studied 1,2-dichloroethane and tetrachloroethylene, which have boiling points of 83 °C and 121 °C, respectively. These were among the chlorinated hydrocarbon compounds found in the marine fuel contamination incident mentioned earlier. Wu et al. [9] discovered that at a temperature of 400 K (127 °C) or more, the studied gaseous organic chlorides are able to spontaneously form hydrogen chloride gas. The authors pointed out that hydrogen chloride gas can form hydrochloric acid when dissolved in water.

The US-based National Research Council (NRC) [10] also states that hydrogen chloride dissolves easily in water and forms hydrochloric acid. The NRC adds that, due to the hygroscopic nature of hydrogen chloride, hydrogen chloride in the air is an aerosol of hydrochloric acid. The amount of water in heavy fuel oil (HFO) is restricted to a maximum of 0.50 volume percentage [6]. Therefore, there is a possibility that chlorinated organic compounds, especially 1,2-dichloroethane and tetrachloroethylene, form hydrochloric acid in the fuel pump of an HFO-fueled engine. Furthermore, according to Bee [4] and CIMAC [2], the chlorinated organic compounds that were found in the mentioned marine fuel contamination case can form hydrochloric acid when subjected to a combination of high temperature and pressure plus the shear forces in an engine's fuel pump.

Several studies have investigated different metallic materials' resistance to hydrochloric acid [11–14]. Many metallic materials are corroded in hydrochloric acid [15,16]. Hydrochloric acid is a strong acid and can cause comprehensive corrosion and pitting corrosion [15]. It can cause stress corrosion cracking in stainless steel [15]. Moreover, reactions between hydrochloric acid and most metals release hydrogen gas [17]. Selecting material resistant to hydrochloric acid is harder than selecting material resistant to sulfuric acid [15]. Corrosion behavior is affected by both the used material and the environment in which the material is being used [18]. This is particularly relevant when choosing metallic materials resistant to hydrochloric acid [15].

The most damaging chemicals in refineries are hydrogen sulfide and hydrogen chloride [19]. Hydrogen chloride is also highly aggressive towards many construction materials [19]. A crude oil's salt content varies and is partially dependent on the source of the oil [20]. These salts mainly consist of sodium chloride, but calcium chloride and magnesium chloride are present too [20]. The mentioned inorganic chlorides can form hydrogen chloride in refineries, which can further produce hydrochloric acid [19]. Crude oil is handled with desalting systems so that the oil is able to meet the acceptable amounts of salt and water [20]. Wu et al. [21] studied desalted crude oil and discovered that most of the total chlorine concentration was composed of organochlorine compounds. Organic chlorides dissolve in oil, and electric desalting devices are not able to remove non-extractable organic chlorides [22]. Organic chlorides can also generate hydrochloric acid under certain conditions [9,21,22]. According to Mitra et al. [23], chloride-containing additives such as chloride-containing surfactants are added to assist extracting the oil. Therefore, it is possible that chlorinated organic compounds are found in fuels and that they can cause similar damages to vessels as in refineries through possible hydrochloric acid formation.

Refineries have set a limit of 1 ppm for organic chlorides [23,24]. The company Capline System has upper limits for organic chlorides, which are 1 ppm in whole crude and 5 ppm in 400 °F (200 °C) end-point naphtha cut [25]. CIMAC [2] stated that marine fuels should have a limit for COCs, defined as having a total organic chlorine content not exceeding 50 mg/kg when measured with standard EN 14077. Rezaee et al. [24] investigated 23 high-sulfur fuel oil samples containing organic chlorides in the range of 0–6666 ppm. On behalf of Viswa Labs, the authors' conclusion was to recommend a gas chromatography–mass spectrometry (GC-MS) analysis of the fuel to test its organic chloride level and, thus, its usability. Rezaee et al. suggested that the concentration of organic chlorides in marine fuels should not exceed 40 mg/L and that the concentration should not exceed 40 ppm in low-viscosity fuels. Wu et al. [21] measured organochlorine concentrations in different petroleum fractions extracted from desalted crude oil. They noticed that organochlorine concentration was approximately 6.5 mg/L for the light diesel fraction and 10 mg/L for the residual oil fraction. Although both values are less than the recommendation of Rezaee et al., both could form hydrochloric acid if the fractions are used as a fuel.

Normally, the working conditions determine the material selection [15]. Marine fuel should not contain inorganic acids [6] (Annex E), and, as indicated earlier, they should contain little or no organic chlorides. Thus, the existence of hydrochloric acid is not considered in the material selection of engine components. However, certain kinds of fuel contaminants introduce a risk of hydrochloric acid formation in the engine system.

The present study investigated the potential harm to metals used in the engines of marine vessels caused by fuel contaminated by hydrochloric acid. The testing was designed to represent an event where hydrochloric acid had already formed in the fuel. The metals chosen for this study were carbon steel, stainless steel, a chromium–molybdenum alloy (CrMo) tempering steel, and aluminum. The used fuel was light fuel oil (LFO). Fuel batches were made with pure hydrochloric acid at concentrations of up to 600 ppm. A water–diesel solution was made for comparison. Metal samples were partially immersed in the fuel samples and kept there for approximately one month. Elemental analysis for samples containing small hydrochloric acid concentrations was performed twice during the study. Several fuel properties were also measured to investigate how they were affected by hydrochloric acid. Additionally, the fuels and metal samples were visually evaluated during the test.

2. Materials and Methods

The fuel used in this experiment was light fuel oil (LFO) that was purchased from a local gas station. The LFO fulfilled the requirements for automotive fuels.

The used hydrochloric acid (HCl) was made with a Titrisol ampoule and deionized water. The hydrochloric acid concentration was approximately 5 M (five molar). Hydrochloric acid was added to the LFO to produce pure hydrochloric acid concentrations of 0 ppm, 25 ppm, 50 ppm, 75 ppm, and 600 ppm. The used hydrochloric acid was a water-based solution. An additional water–diesel sample (H₂O-LFO) was prepared in order to rule out water as a cause of corrosion. The water content in the water–diesel sample matched the water content in the 75 ppm acid–diesel sample. Table 1 lists the measured masses and calculated concentrations for the prepared fuel samples.

The selected metals were carbon steel (CS; grade Imatra 550); stainless steel (SS; 1.4301/1.4307); tempering steel (CrMo; MoC210M/25CrMo4SH); and aluminum (Al; AW-AlSi1MgMn/AW-6082). Table 2 lists their elemental compositions, based on the ingredient certificates. According to Teräskirja [26], steels are composed mostly of iron (Fe). The other elements in the studied metals were copper (Cu), manganese (Mn), silicon (Si), vanadium (V), lead (Pb), carbon (C), chromium (Cr), nickel (Ni), molybdenum (Mo), magnesium (Mg), and zinc (Zn).

Table 1. Measured masses (m) and calculated concentrations (c) for the prepared fuel samples.

Sample	m (LFO) [g]	m (Added Acid, Measured) [g]	m (Calculated Water) [g]	c (Calculated HCl) [ppm]
0 ppm	795.1	0	0	0
25 ppm	633.6	0.11	0.09	29
50 ppm	626.9	0.19	0.16	51
75 ppm	634.5	0.29	0.25	77
600 ppm	633.6	2.31	1.92	602
H ₂ O-LFO	633.9	0.24 *	0.24	0

* added water.

Table 2. Element concentrations of the studied materials.

	Carbon Steel	Stainless Steel	CrMo Tempering Steel	Aluminum
Cu (%)	0.20	0.96	0.20	0.01
Fe (%)	majority	majority	majority	0.20
Mn (%)	1.13	1.66	0.81	0.41
Si (%)	0.24	0.27	0.27	1.07
V (%)	0.06		0.01	
Pb (%)	0.0003		0.0007	
C (%)	0.13	0.023	0.27	
Cr (%)	0.20	18.1	0.99	0.13
Ni (%)	0.15	8.01	0.19	
Mo (%)	0.03	0.29	0.22	
Mg (%)				0.70
Zn (%)				0.01

The metal samples were round bars that were 10 cm long and 2 cm in diameter. They were wiped with a non-frizzing tissue and ethanol and then allowed to dry.

Six samples of 150 mL were taken from each prepared fuel sample and put into a separate borosilicate glass bottle. Each metal bar was partially immersed in a fuel sample, leaving half of the bar in the headspace of the bottle. Polypropylene screw caps were loosely placed on the bottles. The samples were stored in a fume closet due to the possibility of hydrogen gas formation. The metal samples were kept in the fuels for 27 to 29 days.

Density and kinematic viscosity were measured for fuel samples with an acid content of no more than 75 ppm. The used device was an Anton Paar Stabinger SVM 3000 rotational viscometer. The Anton Paar manual [27] states that the device calculates the dynamic viscosity (mPa×s) via the speed of its rotor. The device’s density-measuring cell utilizes the oscillating U-tube principle to determine the density (g/cm³). The kinematic viscosity (mm²/s) is automatically calculated from dynamic viscosity and density. The device makes measurements according to standard ASTM D7042 [27,28].

Distillation properties were measured with PAC’s OptiPMD Micro-Distillation Analyzer. According to its manufacturer [29], the device is able to analyze the distillation properties of, for example, diesel, biodiesel, and gasoline samples which contain at most 20% ethanol. The measurement is in accordance with EN ISO 3405 [29,30]. Distillation properties were measured for fuel samples whose acid content was at most 50 ppm.

The elements dissolved from the metal samples into the fuel were measured with a PerkinElmer 7000 DV ICP-OES spectrometer. The analyzed fuel samples contained at most 75 ppm of hydrochloric acid. Sampling was performed while the metal bars were still in the bottles, and therefore, the bottles were not mixed. The samples were pipetted from the middle of the liquid fuel sample. Because there was a risk that hydrochloric acid could harm the spectrometer, the fuel samples were diluted with kerosene using a weight ratio of one part of fuel sample and seven parts of kerosene. The fuel–kerosene blend was injected into the spectrometer plasma. Calibration was performed with solutions whose element concentrations were known.

The elements measured were Al, Cu, Fe, Mn, Si, V, Zn, and Pb. Element detection is based on an element's specific emitted wavelength [31]. The concentration of the measured element is determined by comparing the measured wavelength intensity with the wavelength intensity of a known element concentration [31]. The used analysis is based on the manufacturer's advice and on standard EN 14538 [32].

Each metal and fuel sample was evaluated visually several times during the test.

The results are arithmetic means of at least two replicant measurements. The relative standard deviations measured for the methods are <1% for kinematic viscosity, <1% for density, and <1.1% for distillation. Quality assurance for ICP-OES spectroscopy analysis was carried out with an internal standard method and by measuring samples with known concentrations.

3. Results

Table 3 presents the density, kinematic viscosity, and distillation properties of the fuel samples at the beginning of the test. Each parameter is compared to standard EN 590 [33] for automotive fuels. The fuel used in this experiment was light fuel oil (LFO) that fulfilled the requirements set in diesel standard EN 590. The density of all fuel samples was 800 kg/m³. The kinematic viscosity for fuel samples containing hydrochloric acid (0 ppm to 75 ppm) was 2.79 mm²/s, and for the water–diesel sample, it was 2.78 mm²/s.

Table 3. Fuel properties of measured fuel samples.

Parameter	0 ppm	25 ppm	50 ppm	75 ppm	H ₂ O-LFO	EN 590 [33] (Class 1)
Density at 15 °C [kg/m ³]	800	800	800	800	800	800–845
Kinematic viscosity at 40 °C [mm ² /s]	2.79	2.79	2.79	2.79	2.78	1.5–4.0
Distillation, % recovered at 180 °C [vol-%]	1.7	2.7	4.8	-	1.4	max. 10
% recovered at 340 °C [vol-%]	95	95	95	-	94	min. 95

The tested hydrochloric acid–diesel samples fulfilled the requirements set for distillation in standard EN 590 [33]. This stipulates that a maximum of 10 vol-% has to be recovered at 180 °C, and a minimum of 95 vol-% has to be recovered at 340 °C. For all tested fuel samples (i.e., excluding those with an acid content of more than 50 ppm), the recovery at 180 °C was below 5 vol-%: at 340 °C, every acid–diesel sample was at the 95 vol-% recovery limit. Only the water–diesel sample did not fulfill the recovery requirement at 340 °C, but its value of 94 vol-% was close to the limit and may be explained with measurement accuracy and the rounding of the value.

Figure 1 depicts the initial boiling points of the measured fuel samples. The boiling point declined with an increase in the concentration of hydrochloric acid, falling from 174 °C in the sample without hydrochloric acid to 157 °C in the sample with 50 ppm hydrochloric acid.

The elements dissolved from metal samples to the fuel samples were measured twice during the test after 13 days and after 27 days. The measured elements were Al, Cu, Fe, Mn, Si, V, Zn, and Pb. The concentrations of Al, Mn, V, Zn, and Pb did not change. The measurements showed that only the concentrations of Cu, Fe, and Si changed. Table 4 presents the results for each of the four metal samples.

Silicon (Si) dissolved from every metal sample. After 27 days, the fuel samples that had hydrochloric acid concentrations ranging from 0 ppm to 75 ppm and contained stainless steel, the CrMo tempering steel and aluminum bars, showed Si at a concentration of 2 ppm. Silicon dissolved from carbon steel to the fuel samples containing acid at 50 ppm and 75 ppm. Hydrochloric acid appears to have accelerated Si dissolving from the CrMo

tempering steel and aluminum, because Si was found in the pure diesel only in the second elemental measurement after 27 days.

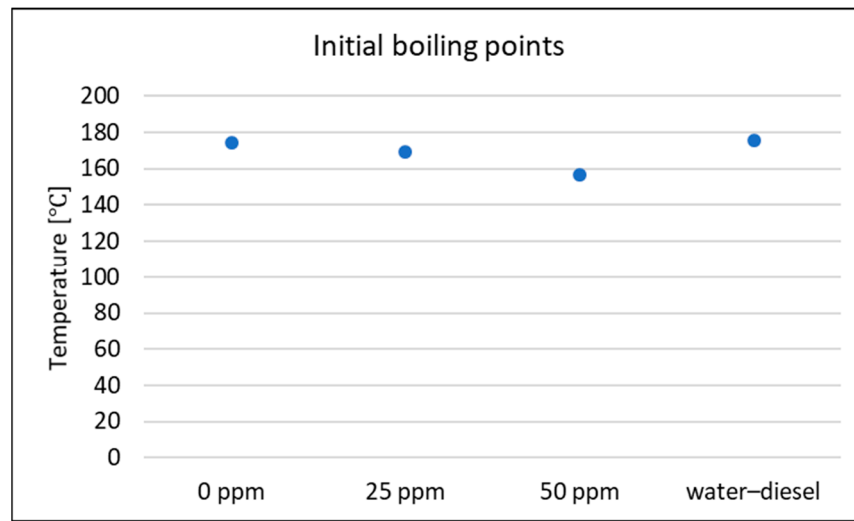


Figure 1. Initial boiling points of fuel samples (acid-diesel 0 ppm, acid-diesel 25 ppm, acid-diesel 50 ppm, and water-diesel).

Table 4. Changes in element concentrations in the fuel samples during the test.

		Carbon Steel			Stainless Steel		CrMo Tempering Steel		Aluminum
		Cu [ppm]	Fe [ppm]	Si [ppm]	Fe [ppm]	Si [ppm]	Fe [ppm]	Si [ppm]	Si [ppm]
Beginning	LFO	<1	<1	<1	<1	<1	<1	<1	<1
After 13 days	0 ppm	1	1	1	1	2	1	1	1
	25 ppm	1	2	1	2	2	2	2	2
	50 ppm	1	2	2	2	2	2	2	2
	75 ppm	1	2	2	3	2	3	2	2
	H ₂ O-LFO	1	1	1	1	1	1	1	1
After 27 days	0 ppm	2	1	1	1	2	1	2	2
	25 ppm	2	2	1	2	2	2	2	2
	50 ppm	2	3	2	2	2	2	2	2
	75 ppm	2	4	2	3	2	5	2	2
	H ₂ O-LFO	2	2	1	1	1	1	1	1

Iron (Fe) was dissolved from every steel bar into the fuel samples containing acid. Fe was also dissolved from carbon steel to the water-diesel sample but not from stainless steel, CrMo tempering steel, nor aluminum. Based on the results in Table 4, hydrochloric acid had an accelerating effect on Fe dissolving from steels. For the fuel with 75 ppm hydrochloric acid, there was an additional effect of time on the concentration in the cases of carbon steel and CrMo tempering steel, as seen in Figure 2. Their iron concentrations rose from 2 and 3 ppm, respectively, after 13 days and to 4 ppm and 5 ppm, respectively, after 27 days. Thus, iron was dissolved from the three steel types under the influence of hydrochloric acid, and this was more pronounced after 27 days for the 75 ppm hydrochloric acid fuel.

The copper concentration in the fuel samples with carbon steel bars showed elevated values at the end of the test. This applied to all fuel samples, including the pure diesel, all hydrochloric acid-enhanced diesel samples, and the water-diesel sample.

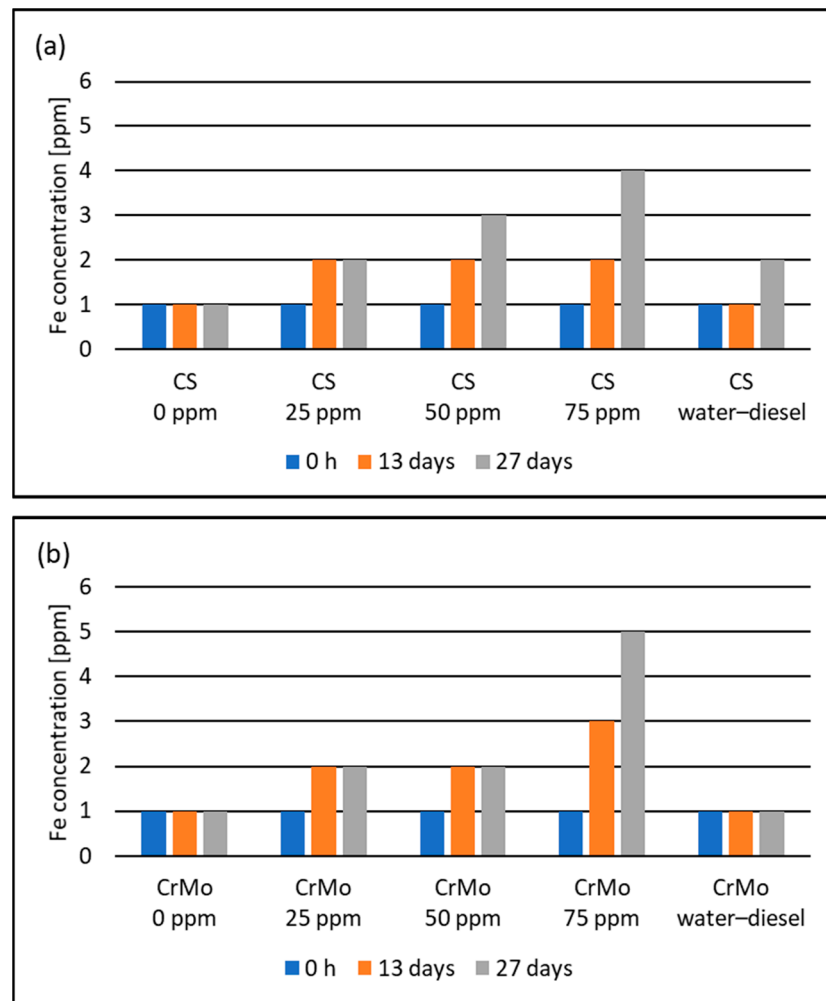


Figure 2. Changes in the measured iron (Fe) concentrations in fuel samples (acid-diesel 0 ppm, acid-diesel 25 ppm, acid-diesel 50 ppm, acid-diesel 75 ppm, and water-diesel) containing (a) carbon steel (CS) or (b) CrMo tempering steel.

Figure 3 shows the metal samples after the test. Every one that was exposed to hydrochloric acid suffered from corrosion. The corrosion was more severe as the acid concentration increased. The metal samples exposed to pure diesel and to the water-diesel blend showed no visible signs of corrosion.

The metal bars were evaluated visually several times during the test. Those in the water-diesel samples showed no signs of corrosion. The only steel from which elements dissolved into the water-diesel sample was carbon steel: Cu and Fe were found at concentrations of 2 ppm at the end of the test. Many steel samples had signs of corrosion already after approximately two days' exposure to the hydrochloric acid-diesel solutions (Figure 4a). In the case of aluminum, visible bubbles formed very quickly on the part of the bar that was immersed in fuel samples with hydrochloric acid at concentrations of 25 ppm, 50 ppm, and 75 ppm. The bubbles formed only on the upper side of the aluminum bar. The higher the acid concentration, the greater the number of bubbles that were formed. The bubbles eventually disappeared during the test. Brown spots were formed on every stainless steel bar that was exposed to fuel with acid (Figure 4b) and on CrMo tempering steels that were exposed to 25 ppm and 50 ppm acid concentrations (Figure 4a). The spots were on the parts of the bars that were in the fuel and were only on the upward-facing sides of the tilted bars.

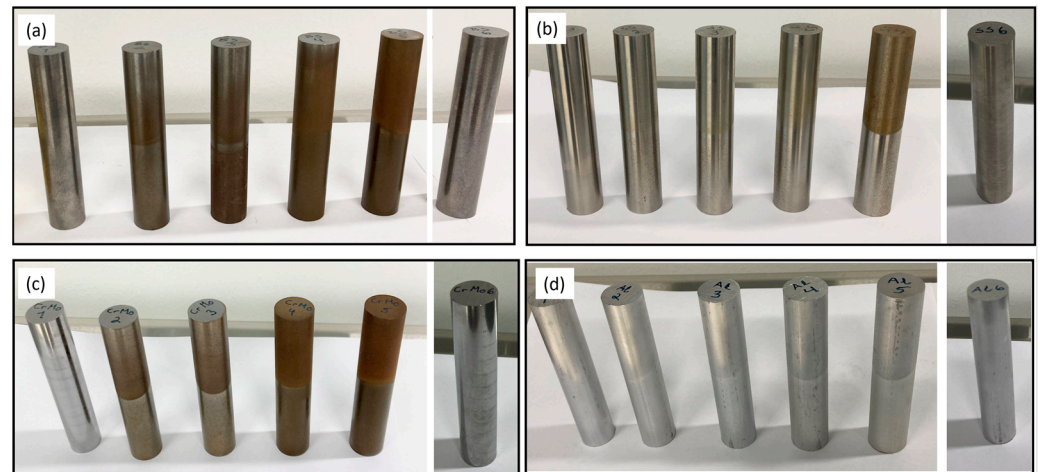


Figure 3. Metal samples after the test: (a) carbon steel; (b) stainless steel; (c) CrMo tempering steel; (d) aluminum. Samples from left to right: hydrochloric acid–diesel 0 ppm; 25 ppm; 50 ppm; 75 ppm; 600 ppm; water–diesel. Bars made of stainless steel, CrMo tempering steel, and aluminum from water–diesel samples were photographed after 27 days; all other bars were photographed after 29 days. The upper part of the metal bars was in the bottle headspace, while the lower part was in the fuel.

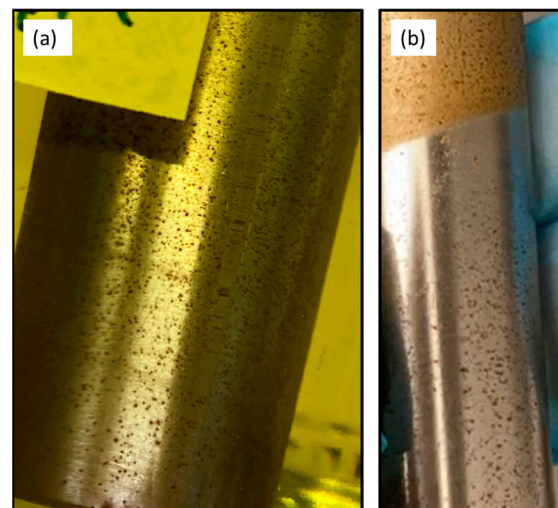


Figure 4. Enlarged pictures of: (a) CrMo tempering steel after 2 days in the 25 ppm acid–diesel sample; (b) stainless steel after 29 days in the 600 ppm acid–diesel sample.

It was noticed that the acid–diesel samples had changed color during the test (Figure 5). The fuel samples that contained CrMo tempering steels and stainless steels changed color in the same way: they were bright yellow in the diesel samples without hydrochloric acid but had become yellow–brownish in the acid–diesel samples. The higher the concentration of hydrochloric acid, the more brownish the fuel became. The fuel samples that contained carbon steels showed discoloration ranging from bright yellow to pale brown and were less clear than the samples with CrMo and stainless steel. All the fuel samples with aluminum bars showed only minor color change which was less intense than that of the other samples.

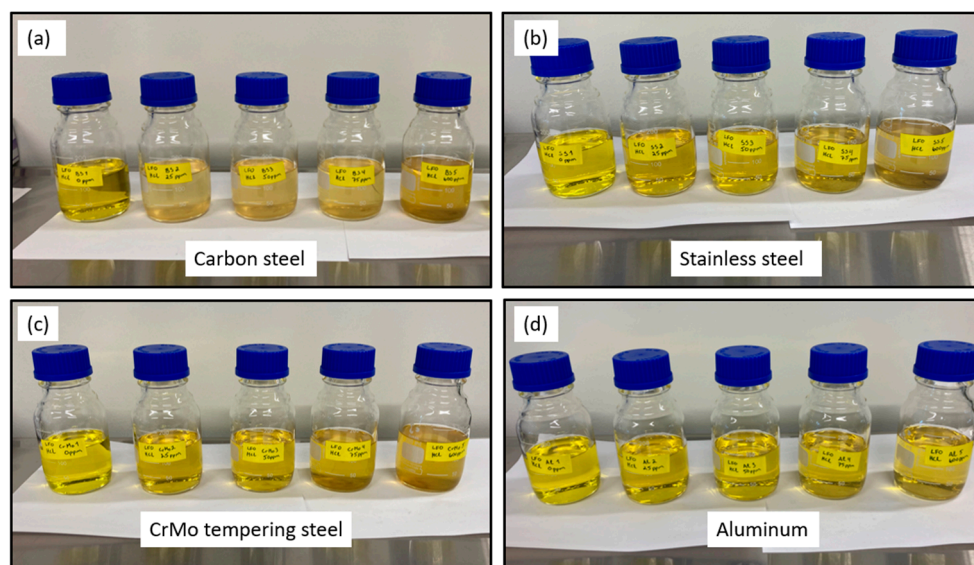


Figure 5. Color change after 29 days of metal bar immersion in fuel samples that contained hydrochloric acid with concentrations of 0 ppm; 25 ppm; 50 ppm; 75 ppm; and 600 ppm (from left to right). Fuel samples that contained (a) carbon steel; (b) stainless steel; (c) CrMo tempering steel; (d) aluminum.

4. Discussion

The combination of materials and the operating environment affects corrosion behavior. Jafar et al. [34] immersed carbon steel samples in different concentrations of hydrochloric acid solutions. The authors concluded that the corrosion rate increased when the concentration of the acid solution increased. They also noticed that the timespan of the samples' weight loss depended on the hydrochloric acid concentration: the higher the concentration, the longer the weight loss continued. Jafar et al. observed that, eventually, the difference in weight loss at different stages of the test almost disappeared in each acid sample. Oguike [35] studied stainless steel Fe6956 in hydrochloric acid. The author discovered that its corrosion rate increased when either the temperature or concentration of the acid was increased. Oguike also concluded that the corrosion reaction of the studied stainless steel in hydrochloric acid solution is spontaneous. Thus, environmental factors such as the temperature and the concentration of the acid have a significant effect on the corrosion resistance of metallic materials.

Hydrogen chloride is one of the most damaging chemicals in refineries [19], and under certain conditions, organic chlorides can generate hydrochloric acid [9,21,22]. Blending organic chloride-contaminated and uncontaminated crude oil is an economically feasible solution for refineries [23]. However, it should be noted that blending does not make the oil free from organic chloride contaminants. Chlorinated organic compounds can form hydrochloric acid, even in an engine's fuel pump [2,4]. Many metallic materials have poor resistance to hydrochloric acid [15,16], and it can lead to serious consequences if such contaminated fuel is used.

There is a possibility that even a small contamination in fuel can cause the deterioration of its properties. Al-Abdullah et al. [36] studied different diesel–gasoline blends, and they noticed that just one volume percent of gasoline in the blend decreases the flash point when compared to pure diesel. Sirviö et al. [37] established that 2 ppm and 4 ppm copper contaminants weakened the oxidation stability of B20 biodiesel–diesel blends. Selim et al. [38] made water-in-diesel fuel emulsions with different water contents, identifying adverse effects on properties including viscosity and density.

The present study investigated the effects of already-formed hydrochloric acid in the fuel on metals used in vessels. The fuel's kinematic viscosity and density did not change in the diesel samples contaminated with hydrochloric acid and water when compared to pure diesel. All the fuel samples fulfilled the requirements set in standard EN 590 for

kinematic viscosity and density at the beginning of the test. The requirements for distillation properties were fulfilled by every measured fuel sample that contained hydrochloric acid. However, the initial boiling points of the fuel samples differed from each other. The initial boiling point declined when the amount of hydrochloric acid in the fuel sample increased. The water content in the fuel samples increased when the amount of hydrochloric acid increased because the added hydrochloric acid was a water solution. Nevertheless, the increased water content alone cannot explain the decline in initial boiling points. The water–diesel sample had a higher water content than the 50 ppm hydrochloric acid sample, and the initial boiling point of the water–diesel sample was higher than in the acid–diesel 50 ppm fuel. The initial boiling point of the water–diesel sample was almost the same as in the pure LFO diesel, and therefore, it was concluded that water alone did not affect the initial boiling point.

The concentrations of the elements Cu, Fe, and Si in the fuel samples rose during the test. Increases in Fe and Si were detected for all three steels (carbon steel, stainless steel, and CrMo tempering steel). For aluminum, only Si concentration increased. Copper dissolved only from carbon steel. After carbon steel immersion, copper was found in the pure diesel, hydrochloric acid–diesel samples, and the water–diesel sample. In previous studies where carbon steels were immersed in B20 fuel blends, it was also noticed that copper was dissolved [37,39]. It seems that copper is easily leached from carbon steel samples.

Every metal bar reacted in some way in the hydrochloric acid–diesel samples within two days of the test starting. At its conclusion, every metal bar that had been in contact with acid had suffered from corrosion. The CrMo tempering steel and carbon steel suffered the most visible damage. Every metal bar that had been in contact with acid had signs of corrosion in parts that were both below and above the fuel surface. Early in the test, aluminum formed bubbles on the part of the bar that was below the surface of the fuel but only on the upper side of the bar. After the test, light dots were noticed in the places where the bubbles had been. Brown spots formed at the same place on the stainless steel and CrMo tempering steels in the 25 ppm and 50 ppm acid–diesel samples. The CrMo tempering steels in the 75 ppm and 600 ppm acid–diesel fuel samples had a brown color on the parts immersed in the fuel. Generally, it was noted for every metal sample that the higher the acid concentration in the solution, the more the metal samples corroded.

Non-noble metals release hydrogen when in contact with acid solutions [40]. Aluminum and iron are non-noble metals [41], and as stated in Table 2, the steels we studied are made mostly of iron. Therefore, it is possible that hydrogen is released when steels and aluminum are in contact with hydrochloric acid–diesel solutions. A chlorine ion (Cl^-) remains when hydrochloric acid (HCl) reacts and releases hydrogen. Chlorine ions react easily and cause pit corrosion [42]. Therefore, it is possible that pit corrosion caused the spots formed on aluminum, stainless steel, and CrMo tempering steel in this study.

The Finnish Institute of Occupational Health [43] states that even substances that evaporate poorly can still form hazardous concentrations in the air. Al-Moubaraki and Obot [19] note that hydrogen chloride is not corrosive when it is dry but very corrosive when mixed with water. The issue of dew-point corrosion in refineries, in most cases, is associated with damage by hydrogen chloride [19]. Therefore, in the present study, it is possible that hydrochloric acid had evaporated from diesel and formed a corrosive gas or an aerosol that corroded the metal bars, even on parts above the fuel surface in the loosely capped sample bottles. The effects of this hazardous gas or aerosol can be best seen with stainless steel immersed in 600 ppm hydrochloric acid–diesel solution: the part in the bottle's headspace clearly corroded more than the part in the fuel.

A. Nelson (Shell Development Co., Emeryville, CA, USA) has created a table of substances that are compatible with pure hydrochloric acid in different temperatures and concentrations of acid (referred to in [17]). Based on this table, pure nickel or molybdenum would be suitable substances to place in contact with hydrochloric acid under the conditions of this experiment. Of the steels investigated in the present study, stainless steel contained the most nickel, i.e., about 8%, compared to <0.2% in carbon steel and CrMo tempering

steel. The 0.29% concentration of molybdenum in stainless steel was also higher than the concentrations in carbon steel and CrMo tempering steel, which were 0.03% and 0.22%, respectively. It should be noted that, according to Kyröläinen [44], the main alloying elements in stainless steel are chromium and nickel. The author states that stainless steel's corrosion resistance is based on a chromium oxide film that forms on the steel's surface. Kyröläinen also notes that adding molybdenum or chromium improves stainless steel's resistance to pit corrosion. Therefore, the amounts of nickel, molybdenum, and also chromium could explain why stainless steel suffered less visible corrosion than the other steels in the present study.

It was also noticed that the fuel samples containing hydrochloric acid changed color when compared to the pure diesel sample. The fuels with stainless steel and CrMo tempering steel bars showed a similar change in coloration and also showed similar levels of Fe and Si. The elevated iron (Fe) concentration may have caused not only the darkening of the fuel samples but also the dark spots on the surface of the CrMo tempering steel and stainless steel bars. The color change in the fuel samples that contained carbon steel also could have been caused by the dissolved Fe found in the fuel samples. Moreover, these fuel samples were the only ones that contained copper (Cu) too. Copper could be the reason why these fuel samples had a slightly lighter color change than the fuel samples that contained stainless steel and CrMo tempering steel. This finding is supported by the study by Sirviö et al. [37], who found that biodiesel–diesel blends containing copper changed color.

The color change in the fuel samples containing aluminum bars cannot be explained by the results from the trace element analysis. All those with hydrochloric acid concentrations between 0 ppm and 75 ppm contained only Si with the same concentration. The only difference between these fuel samples is in their concentrations of hydrochloric acid. Therefore, it is possible that the hydrochloric acid itself, or its reaction with the diesel, caused the color change in the fuel samples. However, aluminum and the steels contain elements (Cr, Ni, Mo, and Mg) whose concentrations in the fuel samples were not analyzed in the present study. Thus, it remains unknown whether these elements were dissolved and could have contributed to the color change of the fuel samples. Nevertheless, it can be noted that the strongest color change was in the fuel samples containing 600 ppm hydrochloric acid.

A review by Mitra et al. [23] gives an account of organochloride compounds contaminating crude oil. In one part of the refinery, organic chlorides had hydrolyzed and formed hydrochloric acid. Not all organochloride compounds hydrolyzed at this point, but they eventually did so in another part of the refinery. Thus, organic chlorides hydrolyzed in two different locations of the refinery. The authors report that the hydrochloric acid from the first hydrolysis caused severe corrosion. The second hydrolysis caused severe corrosion, and the low pH led to a leak in a carbon steel tube. The leak finally resulted in 60–80% of metal loss [23].

A concentration of up to 6000 mg/kg of individual chlorinated organic compound (COC) was found in one marine fuel contamination case [2]. This is ten times the concentration of the 600 ppm acid–diesel solutions tested in the present study, and the metal samples in those suffered greatly from corrosion. The other hydrochloric acid concentrations that were studied were significantly smaller than 600 ppm but still enough to cause corrosion in the studied metals. CIMAC suggested a limit of 50 mg/kg for COCs [2], and Rezaee et al. [24] recommended that organic chlorides in the fuel should not exceed 40 ppm. Also, the Maritime and Port Authority of Singapore (MPA) [45] has issued recommendations for marine fuel to be delivered as a bunker in their port, with the recommendation that residual marine fuel should not contain COCs and that the minimum concentration of total COCs should not exceed 50 mg/kg. COCs levels should be tested according to standard EN 14077, and the testing enhancement is to be adopted from 1 June 2024 [45]. But damage was noticed on the studied metals even at 25 ppm concentration of hydrochloric acid in the present study. It should be noted that all COCs will not necessarily form hydrochloric acid, but it can be assumed that the more COCs are present in the fuel, the more hydrochloric

acid can be formed. The formation of hydrochloric acid is also affected by the amount of water available.

As noted earlier, standard ISO 8217 states that the fuel should not be harmful for machinery nor personnel [6]. Also, standard EN 590 states that “Diesel fuel shall be free from any adulterant or contaminant that may render the fuel unacceptable for use in diesel engine vehicles” [33]. Marine fuels and automotive diesel have been standardized so that the fuels are as safe as possible to use. However, fuels can become contaminated, and a contaminated fuel can cause harm to engines. For example, Wu et al. [21] found organochlorine compounds from the light diesel fraction and residual oil fraction of a desalted crude oil. The detected amounts were under the limits recommended by CIMAC [2] and Rezaee et al. [24]. There is the possibility of hydrochloric acid formation in the fuel system of a vessel. The long-term exposure of fuel system materials to even small concentrations of hydrochloric acid needs still to be studied to evaluate far-reaching effects for vessel engines.

5. Conclusions

This study investigated how fossil diesel fuel already contaminated with hydrochloric acid affects the fuel’s physical–chemical properties and how it affects some metals used in diesel engines. Fuel samples were prepared with concentrations of hydrochloric acid of 0 ppm, 25 ppm, 50 ppm, 75 ppm, and 600 ppm. A water–diesel sample was also prepared for comparison to rule out the possibility of water as a cause of corrosion. Carbon steel, stainless steel, CrMo tempering steel, and aluminum bars were immersed in the fuel samples. The samples were stored at room temperature for approximately one month and were evaluated visually during the test. The fuel samples’ densities, kinematic viscosities, and distillation properties were measured at the beginning of the test. Fuel samples that contained no more than 75 ppm of hydrochloric acid were analyzed twice during the test, identifying dissolved elements from metal samples. The hydrochloric acid–diesel 600 ppm samples were only evaluated visually.

The following conclusions can be made based on the performed study:

- All metal samples reacted within two days in the fuel samples containing hydrochloric acid.
- Even the smallest amount of hydrochloric acid (25 ppm) in the fuel was enough to corrode the metal samples.
- Moreover, corrosion was also noted on parts of the metal samples that were not even in the fuel but in the headspace of the bottle.
- The initial boiling points declined when the concentration of hydrochloric acid increased in the fuel samples.
- Water in diesel fuel had no visible effects on the corrosion of the metal samples.
- It was also observed that the fuel samples containing hydrochloric acid changed color during the test.

In future research, the critical concentration of hydrochloric acid at which the degradation of metal begins should be determined since the effects in this study were seen with rather low levels of hydrochloric acid and within a short exposure time. Also, the impact of temperature on the process should be investigated. Last but not least, the long-term effects of contaminated fuel on metals used in engines and fuel systems need to be investigated to verify whether the recommended concentrations of 50 mg/kg COC are adequate for preventing damage. While the occurrence of fuel contamination with COCs or other compounds might not be frequent, the consequences might be very severe for ships with bunkered contaminated fuels.

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