

Tribological performance degradation of cylinder liner-piston rings in marine ammonia engines induced by ammonia contamination of the lubricating oil

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Abstract: In pursuit of decarbonization, ammonia has attracted extensive attention as a zero-carbon fuel for marine propulsion. However, unburned ammonia and associated byproducts will alter the lubrication environment of the cylinder liner–piston ring (CL-PR) friction pair and induce abnormal damage, while the underlying mechanisms remain unclear. Hence, reciprocating friction tests were

conducted under simulated service environments in ammonia marine engines using lubricating oils with varying ammonia contamination forms and concentrations. Based on the integrated evaluation of friction behavior, wear characteristics, lubrication condition, vibration response and mechanical properties, the results indicate that ammonia contamination universally degrades tribological performance, with ammonia solution exerting a more detrimental effect than ammonia gas, and the severity increasing with ammonia concentration. The introduction of ammonia gas primarily weakens oil film integrity and additive anti-wear performance, thereby intensifying mechanical wear. In contrast, the introduction of ammonia solution deteriorates the anti-wear effectiveness of additives, promotes localized starvation and interfacial corrosion, and induces the formation of extensive corrosion products. These effects collectively result in surface softening, stress concentration, and aggravated spalling, leading to a drop of over 40% in elastic modulus and hardness, with an increase of up to 2.7-fold in wear rate compared to fresh oil, ultimately driving the interfacial damage toward a corrosive-wear coupling effect associated with low-strength corrosion layers. These findings reveal the influence of ammonia contamination on the evolution of CL-PR tribological performance, providing a theoretical basis for optimizing lubricant formulations and improving anti-wear design of tribological components in marine ammonia engines.

Keywords: Marine ammonia engines, Cylinder liner-piston ring, Ammonia contamination form, Oil film thickness, Tribological performance

1 Introduction

Serving as the vital artery of the global economy, the shipping industry is responsible for over 80% of global trade transportation [1]. However, it is also a significant source of greenhouse gas (GHG) and air pollutant emissions [2]. In response, the International Maritime Organization (IMO) has established an ambitious emission reduction strategy targeting net-zero GHG emissions from international shipping by around 2050 [3]. In this framework, the development and deployment of low or zero carbon marine fuels have become crucial pathways for the shipping industry's green transition [4]. Among the various alternative fuels, since ammonia molecules contain no carbon atoms, their combustion in engines does not produce any carbon dioxide, enabling zero-carbon emissions [5,6]. Hence, the use of ammonia as a marine fuel has garnered substantial attention from shipping industries and engine manufacturers [7,8].

Although ammonia is a promising zero-carbon fuel, its introduction poses serious challenges to the reliability of marine engines, an area that has received considerably less attention than combustion and emission investigations [9,10]. The root of these challenges lies in ammonia's inherent properties. As an alkaline and highly reactive gas, ammonia fuel generates substantial amounts of moisture during combustion and often leaves unburned ammonia [11]. During actual engine operation, ammonia may directly enter the lubricating oil, resulting in gaseous ammonia contamination. In addition, it can combine with moisture to form aqueous ammonia solutions that condense in low-temperature regions or directly mix into the lubricating oil, leading to aqueous ammonia contamination [12]. Critically, both gaseous and aqueous ammonia contamination may interact with key additives in lubricating oil (e.g. detergents and anti-wear agents), forming the ammonia-contaminated oil and compromising their effectiveness [13,14]. Agocs et al. investigated the effects of ammonia and NO_2 on lubricating oil performance, observing amination reactions and the formation of amine compounds. Even trace concentrations of ammonia could trigger the generation of insoluble products [15]. Rao et al. examined the interaction between marine cylinder oil and ammonia gas or solution, revealing that free OH^- ions preferentially react with metal-based additive ions to produce insoluble precipitates. A mere 1% mass fraction of ammonia solution was found to induce extensive flocculent precipitation of oils, resulting in additive depletion and reduced oil fluidity [14]. As a result of the complex interactions between ammonia, its combustion products, and lubricating oil, ammonia-contaminated oil is formed, inevitably altering the lubrication environment for critical frictional components (e.g., cylinder liner and piston ring) in ammonia-fueled engines.

The CL-PR assembly, as the core friction pair in marine ammonia engines, is particularly vulnerable to this altered lubrication environment [16,17]. Previous studies indicated that even a minor fuel transition, such as from high-sulfur to low-sulfur fuel, could alter the lubrication environment in engines. It subsequently led to abnormal wear in CL-PRs, ultimately compromising operational reliability [18,19]. Consequently, the significant chemical alterations caused by ammonia contamination are anticipated to have a considerably more severe impact. For instance, Obrecht et al. reported a significant rise in crankcase pressure and elevated levels of metallic debris (Fe, Ni) in used oils during ammonia engine tests, with engine disassembly revealing severe adhesive wear on the CL-PR pairs [20]. Xu et al. demonstrated that the ammonia solution dispersed in 15W-40 engine oil promoted micro-electrolytic reactions on the liner surface, leading to the formation of $\text{Fe}(\text{OH})_3$, and the wear mechanisms were abrasive and corrosive wear [21,22]. Collectively, these studies confirm that ammonia exposure severely degrades the performance of the CL-PR friction pair.

Despite the acknowledged reliability issues associated with ammonia engines, the tribological performance degradation of CL-PRs remains elusive. Existing studies, although valuable, are constrained by several critical limitations. At present, most investigations treat ammonia as a unified factor without accounting for critical variables, such as the introduction form and the contamination degree of the introduced ammonia. Furthermore, existing research focuses on analyzing final wear outcomes, with insufficient attention given to the transition of lubrication states from the oil film. Most consequentially for marine application, the current tribological studies in ammonia engines are confined to automotive lubricants (e.g., 15W-40 oil) with a primary focus on the functional behavior of ZDDP-based additives, thereby limiting their applicability and guidance for cylinder oils dominated by detergent in marine engine applications.

Hence, the lubrication environment of the CL-PR in marine ammonia engines was simulated using cylinder lubricating oil, and a series of friction tests were conducted using materials representative of marine cylinder liners and piston rings. Then, real-time measurable parameters, such as friction coefficient, oil film thickness, and vibration signals were analyzed. In addition, surface morphology, elemental distribution, and oil particles were examined. By comprehensively integrating these findings with the chemical compositions and mechanical properties of the worn surfaces through mechanistic analysis, alongside previous research on the interaction between cylinder oil and ammonia, the effects of ammonia contamination on the tribological properties of the CL-PR friction pair were elucidated. In this context, the objective of this study was to

elucidate the friction and wear mechanisms of the CL-PR friction pair in marine ammonia engines considering multiple factors, thereby providing a theoretical foundation for anti-wear of the CL-PR assembly in marine ammonia engines.

2 Materials and methods

2.1 Materials

To explore the effects of ammonia contaminated oil on the tribological properties of the CL-PR friction pair, this study employed cylinder liners and uncoated piston rings from the MAN B&W 6S50ME marine engine (Yichang Marine Diesel Engine Co., Ltd., Yichang China) as base frictional materials. These engine materials exhibit excellent wear resistance under normal operating conditions, with their specific compositions detailed in Table S1. The cylinder liner and piston ring were prepared via wire-cutting. The cylinder liners were machined to dimensions of $120 \times 15 \times 6$ mm (length $\times$ width $\times$ height), and the piston rings were processed into specimens measuring $8 \times 3 \times 5$ mm (length $\times$ width $\times$ height). Further specimens' details are provided in Section 2.2.

In terms of lubricating oil selection, considering the common types used in marine engines and their performance under specific operating conditions, the Castrol 40SX cylinder lubricating oil was selected, a widely adopted lubricant in marine engines. It is formulated from refined base oils, sulfurized calcium dodecylphenate, and some other functional additives. Its detailed compositions are provided in Table S2, and its physical and chemical properties are detailed in Table S3. To simulate the lubrication condition environment of the CL-PR pairs in ammonia engines, the lubricating oil was separately exposed to ammonia gas and ammonia solution. Hence, the ammonia gas was purchased from Wuhan Iron and Steel Group (Wuhan, China) with a purity of 99.9%. Meanwhile, the ammonia solutions were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), at concentrations of 10% and 25%.

2.2 Experimental procedures

Prior to conducting the friction and wear tests, ammonia-contaminated lubricating oils were prepared following the procedure and methodologies detailed in our previous study [14]. As shown in Table 1, various types of ammonia-contaminated oils were listed and subsequently used as lubricating media in the tests.

Table 1 Specific compositions of lubrication media

Groups	Specific compositions of lubrication medium
PLO	Pure lubricating oil
AGO	Ammonia gas + lubricating oil

ASO-10	Ammonia solution with concentrations of 10% + lubricating oil
ASO-25	Ammonia solution with concentrations of 25% + lubricating oil
PAS	Pure ammonia solution with concentrations of 10%

In these oils, AGO was used to simulate oil contaminated by ammonia gas, while ASO was employed to simulate contamination by ammonia and water (also as ammonia solution) in ammonia engines. These conditions encompassed the primary lubrication environments of the CL-PR friction pair in ammonia engines. Meanwhile, it enabled the investigation into the influences of different ammonia contamination forms on the tribological properties of the CL-PR friction pair. Furthermore, ASO-10 and ASO-25 represented the addition of 1 wt% ammonia solution to lubricating oils, with ammonia concentrations of 10% and 25%, respectively. It was used to investigate the effects of varying ammonia contamination degree on the tribological properties of the CL-PR friction pair. Finally, PLO and PAS represented pure lubricating oil and pure ammonia solution, respectively, serving as control groups.

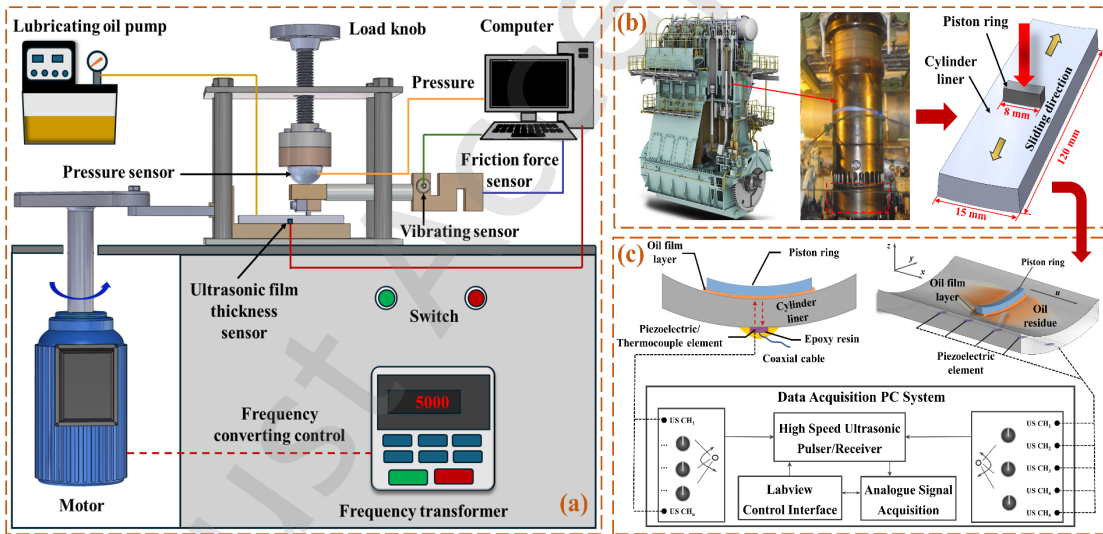


Figure 1 MWF-10 test rig and CL-PR friction pairs: (a) appearance of the frictional test rig, (b) sources of the cylinder liner and piston ring specimens, (c) oil film thickness measurement of the CL-PR friction pair

All friction and wear tests were conducted on the MWF-10 tribometer using a reciprocating sliding configuration, as illustrated in Figure 1. The cylinder liner served as the lower specimen, while the uncoated piston ring was used as the upper counterpart. Both specimens had a surface roughness of $S_q=0.75 \mu\text{m}$. Prior to testing, all specimens were ultrasonically cleaned with petroleum ether and naturally air-dried. Before starting the test rig, lubricants simulating various lubrication conditions were applied to the cylinder liner surface. During the test, lubricating oil was continuously supplied to the

friction pair via an oil pump, with the overall rate maintained at 0.3 ml/min. Tribological tests were performed at reciprocating frequencies of 1.67 Hz (linear velocity of 0.35 m/s) and 3.33 Hz (linear velocity of 0.70 m/s), to simulate the shaft revolutions of low-speed marine ammonia engines. Meanwhile, the normal loads were set at 200 N, 400 N and 600 N, the corresponding contact pressures were 8.3 MPa, 16.6 MPa, and 25.0 MPa, respectively. All experiments were conducted at room temperature. Figure S1 presents the surface temperature of the cylinder liner recorded during the actual friction and wear testing process. Each test lasted 120 minutes, during which coefficient of friction, oil film thickness, and vibration signals were continuously monitored and recorded. The oil film of the friction pair was determined using ultrasonic measurement, and the measurement principle and methodology were elaborated in Section 2.3. Moreover, vibration signals were acquired using an accelerometer (DH5922D, Donghua) at a sampling frequency of 10 kHz. After each test, the lubricating oil used in the experiment was collected and analyzed.

After completing all friction and wear tests, a wear particle monitoring system (Xi'an, China) was employed to analyze the characteristics of wear particles within the lubricating oil. Then, the cylinder liner and piston ring specimens were thoroughly cleaned. The worn surface profile of the cylinder liner specimen was measured using a white-light interferometer (WLI, VR-5200, Keyence, Japan), and the wear rate was calculated according to Equation (1):

$$W = \frac{V}{P \cdot v \cdot t} \quad (1)$$

Where W is the wear rate, V is the wear volume from WLI, P is the normal load, v is the sliding speed, and t is the total time.

Subsequently, the worn surfaces of the cylinder liner and piston ring specimens were examined using scanning electron microscopy (SEM, Tescan, Czech Republic) equipped with energy-dispersive spectroscopy (EDS, Oxford, UK). It provided detailed characterization of the surface morphology and element distribution. Meanwhile, the detailed elemental composition was measured by an X-ray photoelectron spectroscope (XPS, ESCALAB 250Xi, Thermo Fisher Scientific). A Nano indenter (Bruker Hysitron TI980, Germany) was used to characterize the mechanical properties of the worn region. Finally, a comprehensive analysis of the wear mechanisms of the CL-PR friction pair under lubrication conditions contaminated with ammonia was presented.

2.3 Measurement methods of oil film thickness

The oil film thickness is a critical parameter for characterizing the tribological

performance of the CL-PR friction pair. In this study, ultrasonic technology is employed to measure the oil film thickness within the friction pair, which can provide quantitative values of the oil film thickness. The measurement principle of the ultrasonic technology is based on the reflection behavior of high-frequency waves propagating through multi-layer media. When ultrasonic waves travel from the cylinder liner material with higher acoustic impedance, into the lubricating oil film with lower acoustic impedance, partial reflection occurs at the first interface. The transmitted wave proceeds through the oil film and undergoes further reflection at the piston ring interface. These two reflected waves have differences in their propagation paths, resulting in phase shifts or amplitude variations that exhibit a well-defined relationship with the oil film thickness [23]. Figure 2 illustrates the propagation modes of ultrasonic waves through air, lubricating oil, the contact interface between the cylinder liner and piston ring, and the oil film within the friction pair. Then, it can define the reflection coefficient R as the ratio of reflected incident energy at an interface, calculated according to Equation (2):

$$R = \frac{z_1 - z_2}{z_1 + z_2}, z = \rho c \quad (2)$$

Where z represents the acoustic impedance of different media layers, ρ and c represent the density and sound velocity of the medium layers.

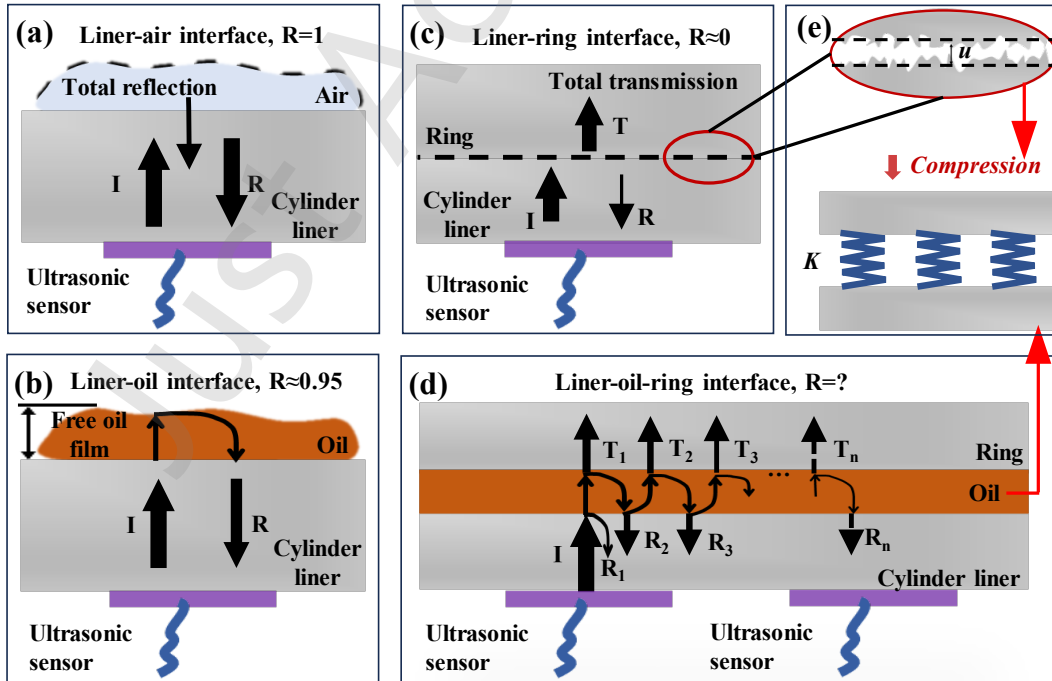


Figure 2 Ultrasonic wave reflection in different media: (a) liner-air, (b) liner-oil, (c) liner-ring, (d) liner-oil-ring, (e) equivalent stiffness model

As illustrated in Figure 2(a), when ultrasonic waves propagate from the cylinder

liner into air, total reflection occurs due to the significant acoustic impedance mismatch. According to the definition of the reflection coefficient, $R \approx 1$ under such conditions. In contrast, when ultrasonic waves travel from the cylinder liner into the piston ring, both being metallic materials with minimal impedance difference, the R is nearly zero, as shown in Figure 2(c). When an oil film forms between the cylinder liner and the piston ring, the system becomes a three-layer structure, leading to partial reflection and partial transmission of the ultrasonic waves. These waves undergo multiple reflections at the upper and lower interfaces of the oil film, generating a series of overlapping echo pulses in the time domain, as depicted in Figure 2(d). Furthermore, the oil film at the interface has a thickness much smaller than the ultrasonic wavelength. Therefore, an equivalent stiffness model can be employed to evaluate the oil film thickness, where the oil film is represented as an elastic spring, as shown in Figure 2(e), with its stiffness K directly correlated to the film thickness. The stiffness K is governed by Equation (3):

$$K = \frac{j\omega(z_1 z_2)}{(z_1 - z_2) - R_2(z_1 + z_2)} \cdot (R_2 - 1) \quad (3)$$

Where, ω is the angular frequency of ultrasonic waves, R_2 is the reflection coefficient of ultrasonic waves in oil, to be measured.

Subsequently, the film thickness of the CL-PR friction pair can be represented by Equation (4):

$$h = \frac{\rho_2 c_2^2}{K} = \frac{\rho_2 c_2^2}{2\pi f z_1 z_2} \sqrt{\frac{|R_2|^2 (z_1 + z_2)^2 - (z_1 - z_2)^2}{1 - |R_2|^2}} \quad (4)$$

Where, according to the Reference [24], ρ and c of the oil are 858 kg/m^3 and 1472 m/s , respectively. z of cylinder liner and piston ring are 43.29 MRayls and 40.03 MRayls .

According to Equation (4), the oil film thickness can be determined by measuring the ultrasound reflection coefficient in the lubricating oil. Thus, the ultrasonic monitoring configuration and procedure used in our previous research were also adopted in this experiment, and the ultrasonic sensor illustrated in Figure 1(c) was employed to capture the reflection coefficient [25]. To enable accurate measurement of the oil film thickness across different positions of the CL-PR friction pair, five ultrasonic sensors with a rectangular shape of $1.8 \times 5 \text{ mm}$ to match the ring specimens and a center frequency of 10 MHz were installed, while the acquisition rate was set to 500 Hz and the pulse repetition frequency of the ultrasonic waves was set to 5 kHz . Furthermore, to mitigate ultrasonic signal drift induced by temperature, the sensor was calibrated using a reference signal at multiple temperatures prior to experimentation. The amplitude-frequency spectrum was derived by applying a fast Fourier transform (FFT) to the signal of the

reflected wave. The reflection coefficient was then calculated by normalizing the reflected signal from the oil film region against the reference signal, enabling the determination of oil film thickness. Figure S2 shows the complete oil film thickness processing, including the extraction of ultrasonic signal, calculation of the reflection coefficient, and final derivation of oil film thickness.

3 Results

3.1 Friction behavior of CL-PRs

Figure 3 illustrates the average coefficient of friction (COF) of various lubricants under different operating conditions involving multiple loads and reciprocating speeds during tribological testing. Taking the friction-reducing performance of PLO as the baseline, the COF associated with PLO consistently remains at the lowest level. In contrast, the introduction of ammonia contaminants generally leads to deterioration in frictional responses, with the most severe degradation observed under contamination by high-concentration ammonia solute (ASO-25) across most operating conditions.

Specifically, the disparity in frictional responses among lubricants becomes most significant under low load and low reciprocating frequency (200 N-1.67 Hz), increases in COF exceeding 30% are observed for both AGO and ASO-25 relative to the PLO, demonstrating that ammonia contaminants significantly elevate frictional resistance. However, the differences in COF among the lubrication conditions are markedly reduced with increasing load. In particular, the COF values of AGO and ASO-10 gradually approach that of PLO, with the average increase under low-speed conditions decreasing from 34% and 11% to 16% and 5%, respectively, while under high-speed conditions, the values become nearly identical to that of PLO. In contrast, ASO-25 consistently exhibits the highest COF under nearly all operating conditions, with increases ranging from 19.3% to 45.3% relative to PLO, indicating that high concentrations of ammonia contamination substantially intensify frictional resistance. PAS exhibits distinct frictional behavior due to the deviation from conventional oil-lubricated systems and high chemical reactivity. Specifically, PAS demonstrates an exceptionally high COF under low-load conditions, reaching an increase of up to 287% relative to PLO. Nevertheless, as the load increases, the COF decreases rapidly, with a reduction of 21% relative to PLO ultimately observed under severe conditions of low speed and high load (1.67 Hz–600 N).

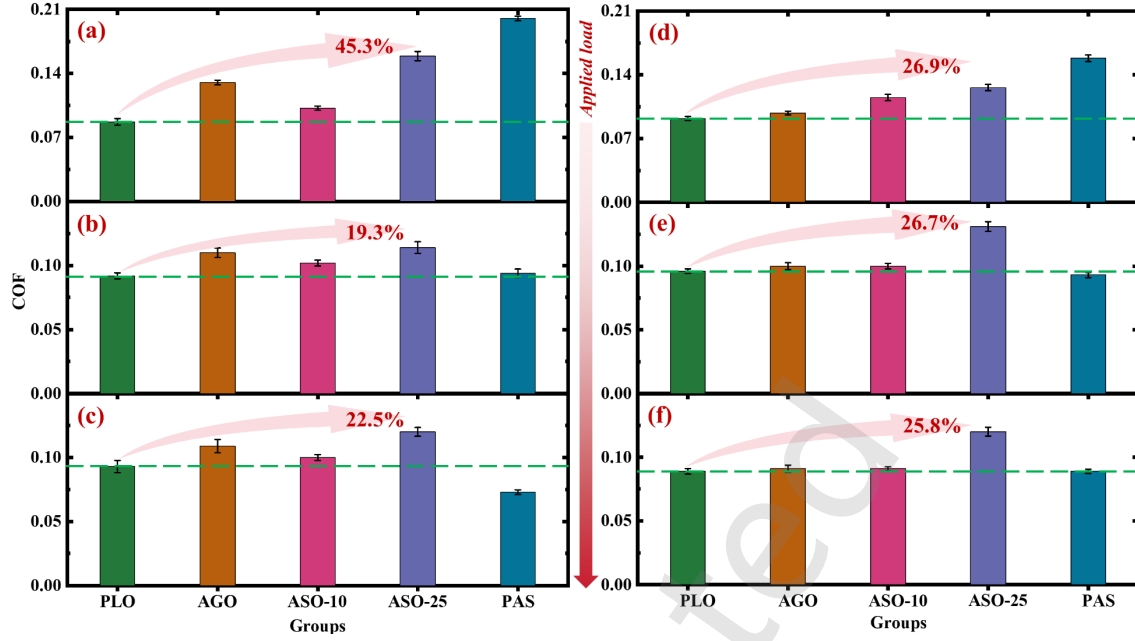


Figure 3 Average COF of CL-PR under different lubrication conditions across multiple conditions: (a) 1.67 Hz-200 N, (b) 1.67 Hz-400 N, (c) 1.67 Hz-600 N, (d) 3.33 Hz-200 N, (e) 3.33 Hz-400 N, (f) 3.33 Hz-600 N

Furthermore, to evaluate the dynamic influence of contaminant ingress on the interfacial friction behavior of the CL-PR system, a comparative analysis was conducted based on the intrusion form and concentration of ammonia contaminants. Specifically, Figure 4 presents the evolution of friction coefficient curves for ammonia gas and ammonia solution contamination. Under most conditions, PLO, AGO, and ASO-25 generally follow a typical tribological evolution pattern, where COF decreases to varying extents after a running-in period and subsequently enters a steady-state regime. This behavior is most evident under low load (200 N), while the COF profiles become less uniform as the load increases, with enhanced high-frequency oscillations and a tendency toward increasing friction during later stages.

Specifically, the frictional state of PLO exhibits high sensitivity to operating parameters. Under extreme conditions, microscopic fluctuations during the steady-state phase intensify, and a pronounced increase in COF emerges in the later stages. In comparison, AGO exhibits higher COF values than PLO while maintaining greater stability in frictional behavior, as reflected by reduced fluctuations in COF during steady-state operation. In contrast, the running-in characteristics of the ASO-25 condition are weakened, with the COF remaining consistently at a high level and exhibiting an upward trend under certain high-load conditions. A notable feature lies in the relatively smooth COF profile, where severe fluctuations are almost absent, indicating a reduced sensitivity of the interface to operational parameters within contaminated interfaces. Notably, PAS

exhibits fundamentally different frictional behavior, characterized by continuous and intense fluctuations without a stable wear stage. Particularly under low-load condition (200 N), the COF curve demonstrates frequent sawtooth-like oscillations and a continuous upward trend over time, ultimately reaching a peak value of approximately 0.24. Such behavior suggests progressive accumulation of interfacial damage, accompanied by a marked deterioration in frictional conditions.

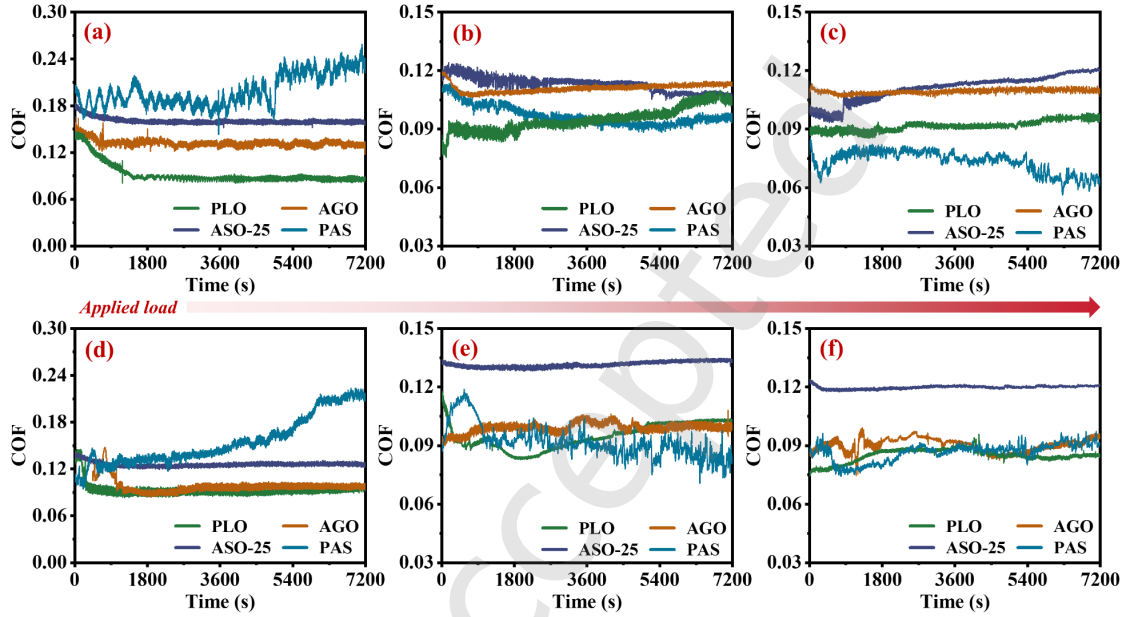


Figure 4 COF variation tendency of CL-PR under different contamination forms across multiple conditions: (a) 1.67 Hz-200 N, (b) 1.67 Hz-400 N, (c) 1.67 Hz-600 N, (d) 3.33 Hz-200 N, (e) 3.33 Hz-400 N, (f) 3.33 Hz-600 N

Figure 5 further presents the COF evolution curves under ammonia solution contamination at varying concentrations, revealing a clear stepwise dependence of frictional response on contaminant concentration. The distribution of COF exhibits a strong positive correlation with ammonia solution concentration across all conditions. Notably, the frictional evolution trends of ASO-10 and ASO-25 are similar, characterized by smoothness and operational stability, indicating reduced interfacial sensitivity to mechanical disturbances. In particular, ASO-10 displays a distinct deviation from the PLO baseline under low-load condition (200 N). However, as the load and reciprocating frequency increase, frictional heating and mechanical shear progressively drive the friction interface toward boundary contact, where the COF evolution of ASO-10 becomes increasingly constrained, gradually converging toward the PLO baseline and nearly overlapping with it during the later stages of testing.

Overall, the macroscopic frictional behavior of the CL-PR interface is governed by multiple factors. Considering that the introduction of ammonia contaminants generally

leads to an increase in lubricant viscosity [14], distinct differences in flow characteristics among lubricants lead to pronounced variations in frictional responses under mild conditions. As the load and reciprocating frequency increase, frictional heating promotes viscosity reduction and convergence among lubricants, resulting in reduced differences in COF and a general increasing trend during later testing stages.

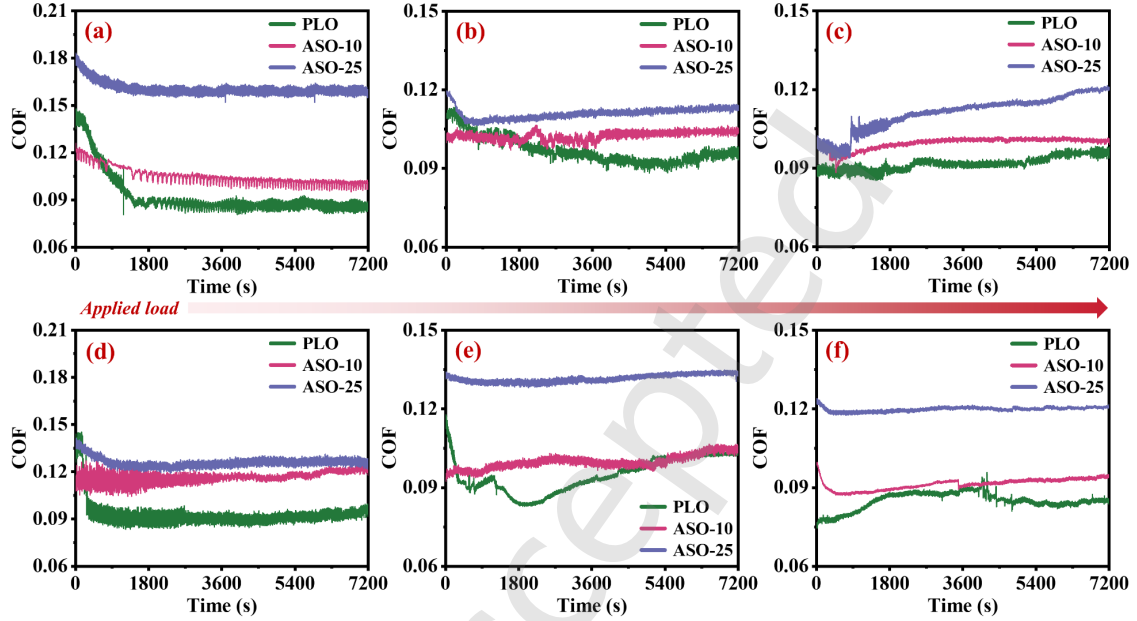


Figure 5 COF variation tendency of CL-PR under different concentration of ammonia solute across multiple conditions: (a) 1.67 Hz-200 N, (b) 1.67 Hz-400 N, (c) 1.67 Hz-600 N, (d) 3.33 Hz-200 N, (e) 3.33 Hz-400 N, (f) 3.33 Hz-600 N

3.2 Wear characteristics of CL-PRs

3.2.1 Wear rate of cylinder liners

As shown in Figure 6, the representative three-dimensional morphologies of the worn liner surfaces under severe operating conditions (1.67 Hz, 600 N) are presented, along with their corresponding two-dimensional cross-sectional profiles. The straight sections of baseline represent the unworn reference plane, and the shaded region indicates the cross-sectional area of material loss. A clear positive correlation can be identified between wear severity, scar depth, and the degree of ammonia contamination. The PLO condition exhibits the slightest wear traces, whereas AGO leads to limited degree of surface damage deterioration. In contrast, the introduction of ammonia solution leads to a substantial deterioration in wear performance. Under ASO conditions, the wear scar depth increases by more than 50% compared with both PLO and AGO, with high-concentration ammonia solution (ASO-25) inducing more severe localized spalling at dead-center regions. Under extreme conditions, the PAS environment results in the greatest volumetric wear loss, where the maximum wear depth approaches 7 μm . This suggests that the negligible

viscosity and high chemical activity of aqueous ammonia may facilitate spalling and may trigger abnormal wear.

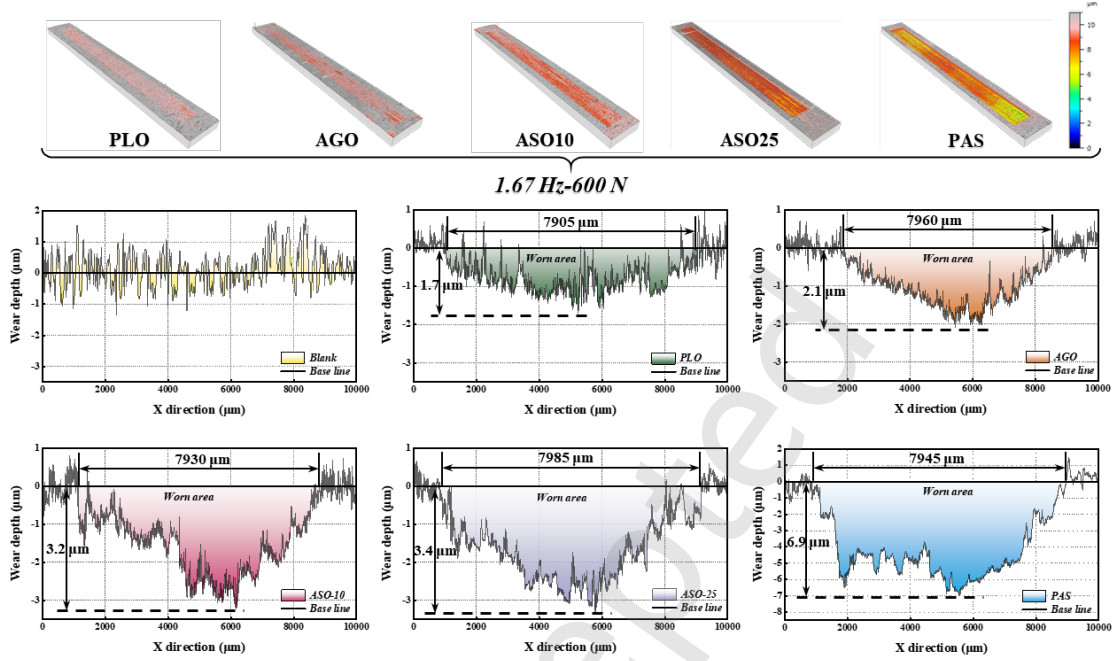


Figure 6 Topography and cross-sectional outlines of the wear tracks under different lubrication conditions at 1.67 Hz-600 N

Figure 7 presents the wear rate of the liner surface under different operating conditions. It can be observed that the wear rate generally follows hydrodynamic principles, exhibiting a positive correlation with normal load and a negative correlation with sliding speed. Through comparative analysis, the PLO condition consistently demonstrates the lowest wear rate, whereas the presence of ammonia contaminants leads to a significant deterioration in wear behavior. In particular, the introduction of ammonia gas (AGO) results in an overall increase in wear rate, though remaining comparable to PLO under moderate loads (200-400 N), but becoming markedly intensified with increasing applied load, rising from 28% under mild conditions (3.33 Hz-200 N) to 134% under severe conditions (1.67 Hz-600 N).

In comparison, the introduction of ammonia solution results in a pronounced increase in wear rate, with the degree of deterioration amplified by higher ammonia concentrations and increased load. Under ASO-25 conditions, the wear rate increases by 72%–274.8% relative to PLO and by 13.1%–89.2% compared to AGO. However, the overall wear behavior remains similar to that of ASO-10, with differences typically within 20%. The most severe wear occurs under PAS conditions, where wear rates exceed 2.6 times those of both PLO and ASO-25, reaching up to eight times higher under certain conditions.

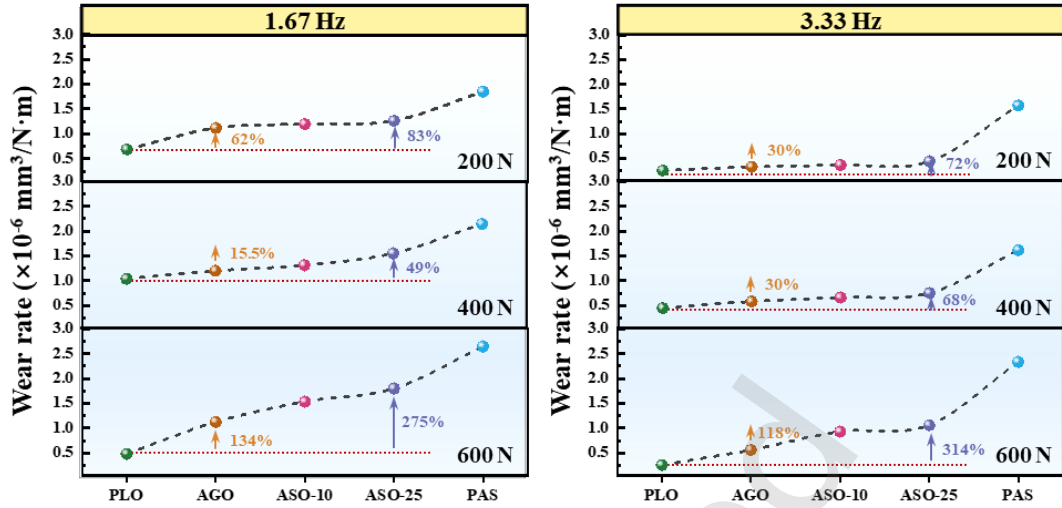


Figure 7 The wear rate of the cylinder liner under different lubrication conditions across multiple conditions

3.2.2 Morphological characteristics and elemental distribution of worn surfaces

Figure 8 presents the representative SEM morphologies of worn liner surfaces across different lubrication environments. As illustrated in Figure 8(b), the wear severity under the PLO condition remains minimal, the original polishing texture is partially smoothed, while shallow micro-ploughing grooves and slight localized deformation along the sliding direction are observed. Meanwhile, patchy and relatively uniform film-like structures can be identified, suggesting that calcium-based additives can provide effective anti-wear performance. Upon the introduction of ammonia gas (AGO), the wear morphology undergoes noticeable deterioration, as shown in Figure 8(c). Distinct layered structures emerge within the wear track, accompanied by micro-cracks, localized spalling, and deeper ploughing grooves, reflecting aggravated mechanical wear.

Furthermore, the transition in damage mode is observed when introducing ammonia solution. Under the ASO-10 condition (Figure 8(d)), ploughing grooves become deeper and wider, while dense distributions of cracks, spalling, and micro-pitting are observed around the grooves, indicating the occurrence of more severe wear accompanied by corrosive damage. With increasing concentration of ammonia solute (ASO-25), the surface damage is further intensified, as illustrated in Figure 8(e). Deep and extensive macro-ploughing grooves traverse the observation field, accompanied by pronounced macro-pitting, dense micro-pitting, large-area delamination spalling, and macro-peeling. These characteristics suggest that the damage has extended into the subsurface, with tribocorrosion emerging as the primary failure mechanism [26]. Regarding the extreme PAS condition, Figure 8(f) reveals that the worn surface is extensively covered by macro-corrosion regions, exhibiting a heavily corroded rough topography. Widespread macro-

spalling, pitting features, and residual corrosion debris are observed, demonstrating that the interfacial damage is dominated by typical corrosive-wear.

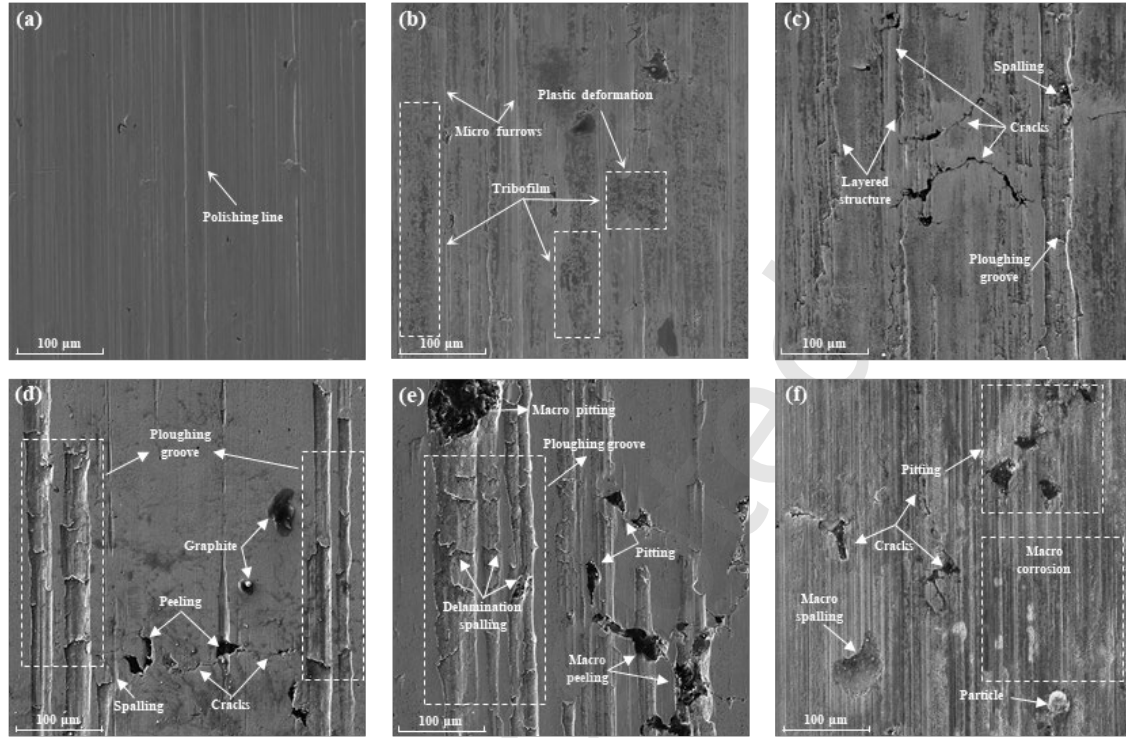


Figure 8 SEM micrographs of the worn liner surfaces across different lubrication conditions under 1.67 Hz-600 N: (a) Unworn, (b) PLO, (c) AGO, (d) ASO-10, (e) ASO-25, (f) PAS

Taking ASO-25 condition as a representative case of severe wear, Figure 9 presents SEM images of the worn surface under various operating conditions. A pronounced nonlinear deterioration in wear morphology can be observed with increasing load and reciprocating frequency. Under a low load of 200 N, the surface morphology is mainly characterized by shallow ploughing grooves, micro-cracks, and localized mild spalling along the sliding direction. This indicates that the limited contact stress and the oil film approaching hydrodynamic lubrication primarily result in slight wear. However, as the load increases to high levels (400/600 N), the surface morphology undergoes a significant evolution into deep ploughing grooves, macro-cracks, and extensive delamination spalling. This morphological transition suggests that high loads likely intensify stress concentration at surface defects, thereby increasing the severity of wear.

Furthermore, an increase in reciprocating frequency further exacerbates the interfacial damage. Morphological comparisons reveal that at low speeds, material removal predominantly manifests as localized surface collapse. In contrast, subsurface crack networks become increasingly dense and interconnected at high speeds, leading to

enlarged and more severe spalling areas. This aggravation can be briefly attributed to the substantially increased contact frequency and cyclic loading, which will accelerate the localized tribochemical reactions and facilitate the initiation and propagation of fatigue cracks due to the deterioration of oil film integrity.

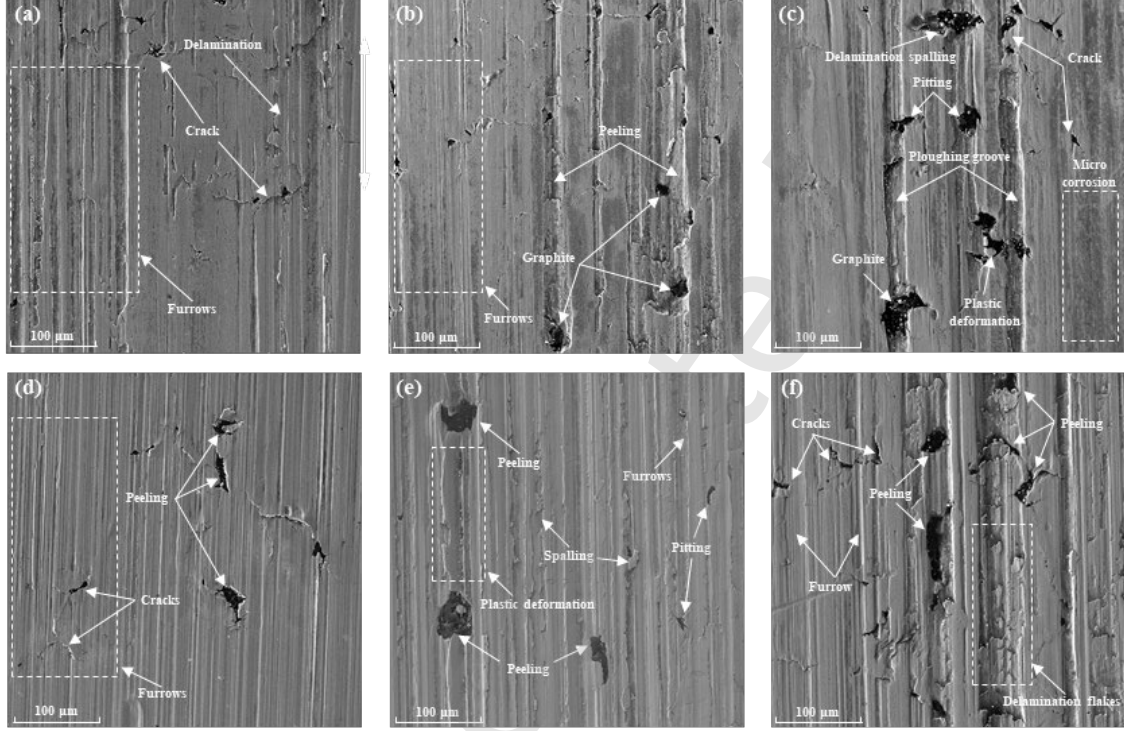


Figure 9 SEM micrographs of the worn liner surfaces with ASO-25 across multiple conditions: (a) 1.67 Hz-200 N, (b) 1.67 Hz-400 N, (c) 1.67 Hz-600 N, (d) 3.33 Hz-200 N, (e) 3.33 Hz-400 N, (f) 3.33 Hz-600 N

To further investigate the wear mechanisms under different lubrication environments and clarify the participation pathways of tribochemical reactions, the elemental distribution within the worn regions was analyzed, as illustrated in Figure 10. The PLO condition serves as a reference for distinguishing normal lubrication and wear behavior, with the surface primarily composed of matrix elements Fe (82.88%) and C (9.13%), while the content of Cu remains relatively low, which is a trace alloying element. A critical feature lies in the presence of Ca (0.34%) alongside the absence of O enrichment. This suggests the effective formation of tribofilms by additives, indicating favorable anti-wear performance.

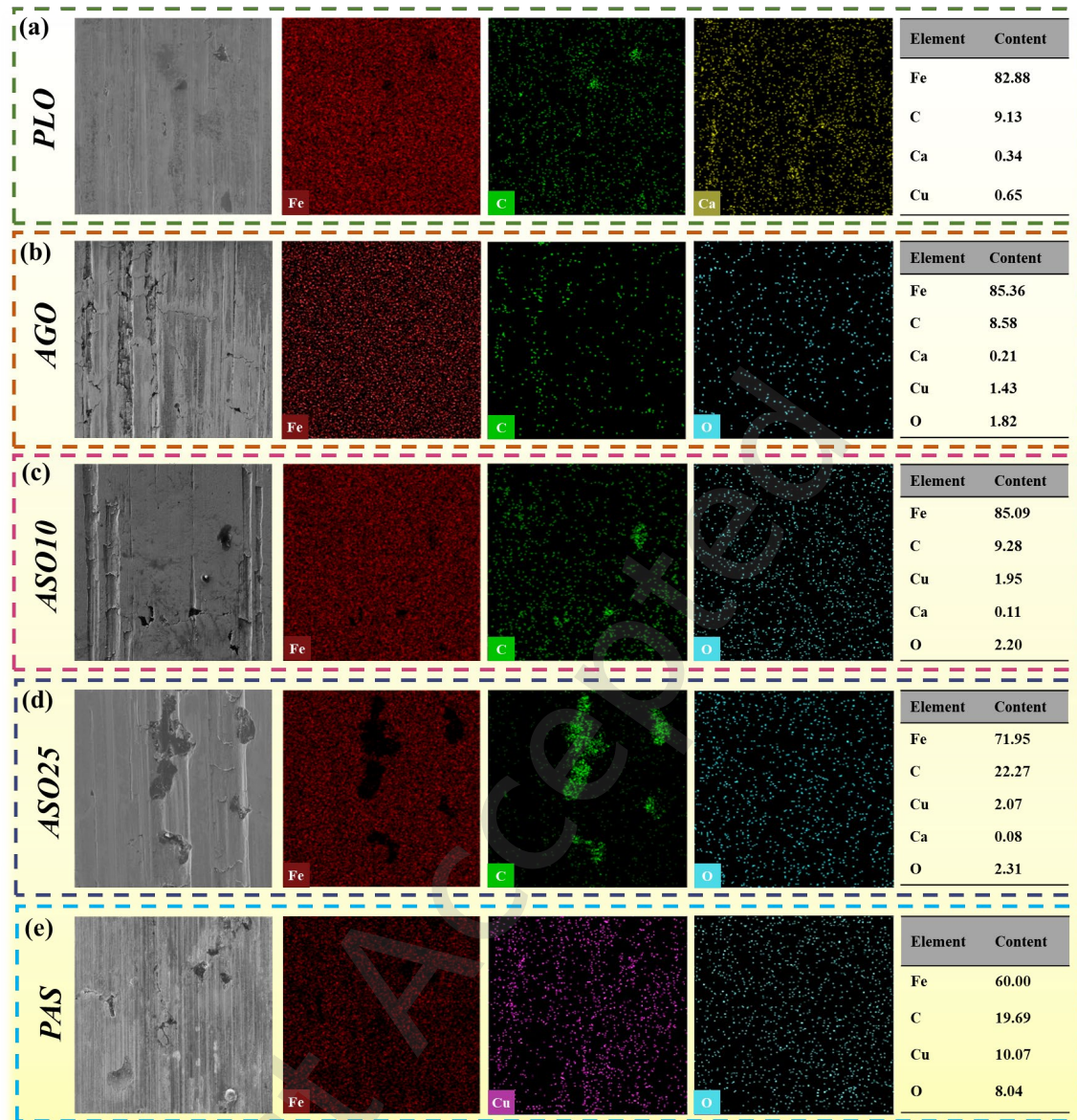


Figure 10 The elemental distribution on the worn liner surface under different lubrication conditions at 1.67 Hz/600 N: (a) PLO, (b) AGO, (c) ASO-10, (d) ASO-25, (e) PAS

In contrast, under AGO and ASO-10 conditions, although the overall contents of Fe and C remain comparable, a critical distinction is observed in the significant reduction of Ca content from 0.34% to approximately 0.21% and 0.11%, respectively. Meanwhile, noticeable enrichment of O (~2%) emerges, accompanied by a marked increase in Cu content. A more pronounced transformation is evident under the ASO-25 condition, where elemental redistribution occurs substantially, with C content increasing abnormally to 22.27%, which is highly concentrated within deep spalling pits and pitting regions, as shown in Figure 10(d). Additionally, O contents exhibit slight increases relative to ASO-10, whereas Ca continues to decline. These observations suggest that the surface layer of the matrix has undergone severe degradation or removal, leading to preferential exposure

and localized enrichment of the subsurface graphite phase. By comparison, PAS condition can be regarded as an extreme reference representing chemically dominated surface failure, where C content reaches 19.69%, O increases significantly to 8.04%, and the sensitive element exhibits substantial enrichment to 10.07%. These features imply the occurrence of dealloying corrosion within the substrate, resulting in segregation of the internal sensitive element toward the surface [27]. Meanwhile, corrosion products accumulate extensively in the form of a loose passive layer, rendering the interface characteristic of a typical corrosive-wear effect.

3.3 Characteristics of Lubrication Condition

3.3.1 Lubrication behavior of friction pairs

To investigate the impact of contaminant intrusion on the load-carrying capacity of the lubricating oil, the ultrasonic measurement technique was employed to quantitatively characterize the spatial distribution of the oil film thickness (OFT) across different lubrication environments, as depicted in Figure 11. Furthermore, to provide a quantitative criterion for interpreting the observed lubrication regimes, we employ the composite roughness parameter S_σ and the typical lubrication margin λ , according to Eq. (5) and (6):

$$S_\sigma = \sqrt{S_{q\ ring}^2 + S_{q\ liner}^2} \quad (5)$$

$$\lambda = \frac{h}{S_\sigma} \quad (6)$$

Where $S_{q\ ring}$ and $S_{q\ liner}$ represent the surface roughness of the piston ring and the cylinder liner respectively, h is the measured oil film thickness. For the applied CL-PR components, a value of $S_\sigma=1.06\ \mu\text{m}$ can be approximately regarded as the critical OFT for judging boundary lubrication, while OFT higher than $3S_\sigma$ ($\lambda>3$) is considered as a sign of entering hydrodynamic lubrication [28].

As shown in Figure 11(a), the OFT profiles of various lubricants at different cylinder liner stroke positions are presented. The transient profile characterized by valley shape reflects the motion trace of the piston ring, where descending and ascending segments represent the processes of entering and leaving the sensor area, while the lowest point within the central valley corresponds to the OFT at the position [29]. Except for PAS, the minimum oil film thickness (MOFT) of all oil-lubricated groups exceeds $1.1\ \mu\text{m}$, indicating the mixed lubrication regime while approaching the threshold of boundary lubrication. Among these, PLO exhibits the lowest overall OFT trend, while the enhancement of hydrodynamic effects remains limited. The thickening response of the oil film is relatively delayed, with an increase of only approximately 10% in OFT from positions S1 to S2, and the maximum OFT at position S3 increases by merely 33%. This

can be primarily attributed to the low apparent viscosity of PLO, which restricts hydrodynamic pressure development.

However, the contamination of ammonia gas (AGO) will increase viscosity through complex formation, leading to enhanced hydrodynamic pressure and a subsequent moderate increase in OFT. The MOFT and maximum OFT of AGO increase by 6% and 5% compared with PLO respectively. Meanwhile, the oil film formation becomes more rapid, the OFT increases by approximately 16% within the acceleration region (S1–S2). Moreover, the introduction of ammonia solution (ASO) induces emulsification and further increases the viscosity. As a result, the overall OFT of ASO-10 and ASO-25 increases by approximately 20% relative to PLO. Since oil film formation is primarily governed by rheological properties, both exhibit similar OFT distributions. In contrast, PAS is characterized by an extremely low viscosity, resulting in an OFT reduction of more than 40% compared to PLO. Consequently, the entire stroke operates under boundary lubrication, with the lubrication mechanism dominated by tribochemical reactions at the contact interface.

Notably, the increase in apparent OFT caused by contaminant-induced thickening does not imply improved lubrication performance. Since ultrasonic signals used to characterize OFT are susceptible to interference, the presence of multiphase contaminants within the oil film may induce acoustic scattering, resulting in pseudo-thickening signals that appear as local distortions and fluctuations in OFT profiles [29]. As illustrated in Figure 11(a), the OFT curves of PLO remain smooth and stable across all positions, indicating stable lubrication. In contrast, contaminated conditions exhibit varying degrees of local distortion and fluctuation in OFT profiles, reflecting the degradation of fluidity.

Specifically, weakened flow replenishment combined with squeeze effects in AGO conditions may lead to localized starved contact near dead-center regions. Comparatively, contamination of ammonia solution exacerbates oil film degradation, with ASO conditions showing intensified distortions in OFT profiles, where interference regions extend toward the mid-stroke, indicating that the effective lubrication region within the frictional interface is significantly reduced. As for PAS conditions, the OFT profiles reveal a highly defective structure of the water film below the boundary lubrication threshold λ , indicating nearly complete lubrication failure across the entire stroke. These observations confirm that the elevated apparent OFT observed in certain contaminated systems may partially originate from interference caused by contaminants and oil-air mixture in ultrasonic measurements, while failing to compensate for the actual deterioration in lubrication performance.

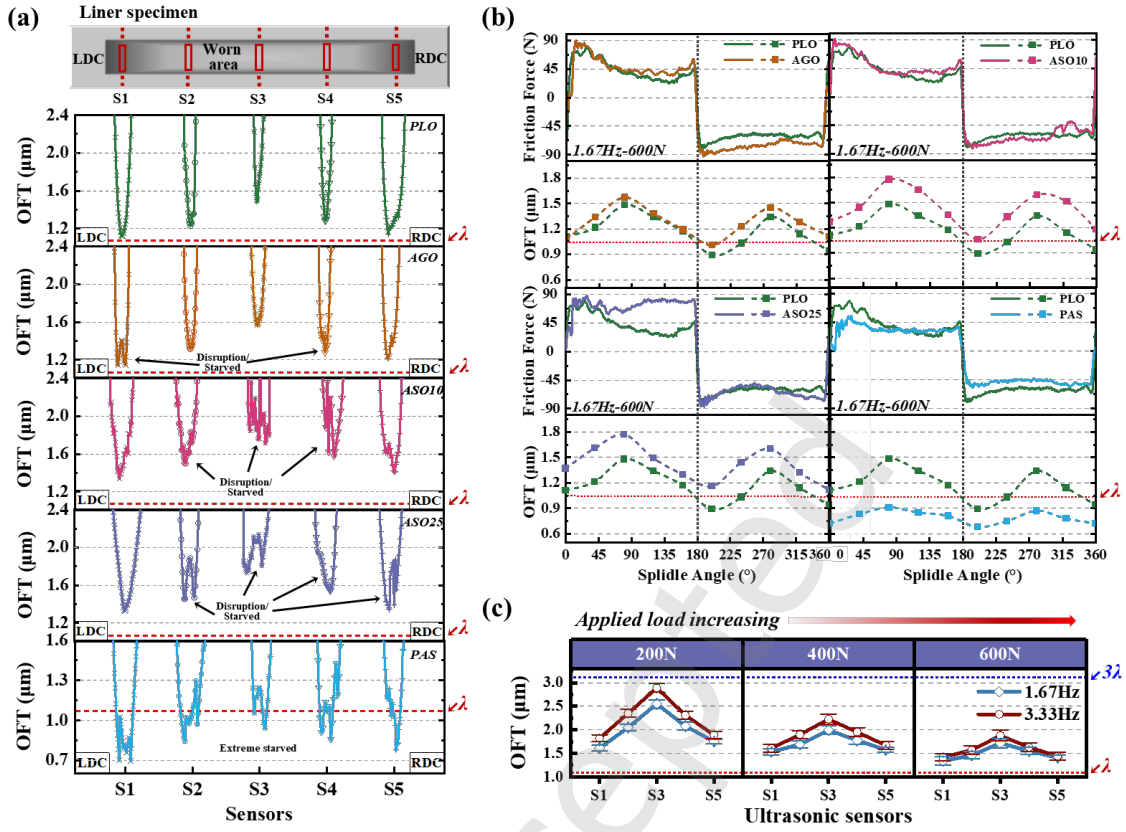


Figure 11 (a) OLF variation trend, (b) Time resolved data of friction force and OLF distributions for CL-PR with different lubricating oils under 1.67 Hz-600 N, (c) OLF distribution over stroke with ASO-25 across multiple conditions

As shown in Figure 11(b), the relationship between lubrication and wear behavior of the CL-PR under various lubrication environments is presented, while Figure 11(c) illustrates the evolution of OLF for the ASO-25 lubricant across all conditions. The lubrication behavior clearly follows classical hydrodynamic principles, where OLF increases nonlinearly with increasing reciprocating frequency and decreasing load. However, even under the most favorable condition (200 N, 3.33 Hz), the maximum OLF remains below the threshold for full hydrodynamic lubrication, indicating that the tribological pair predominantly operates within the mixed lubrication regime throughout the test, with degradation to boundary lubrication occurring in severe regions such as reversal dead centers.

Minor mechanical asymmetry and dynamic imbalance within the reciprocating drive system may contribute to the observed differences between the forward and reverse strokes [29]. Taking PLO as a reference, the system remains primarily in mixed lubrication during the 0–180 $^{\circ}$ CA stroke, whereas boundary lubrication is approached near the dead center during the reversal stroke (180–360 $^{\circ}$ CA). Throughout the entire stroke, the friction force associated with PLO remains the lowest. Under AGO conditions,

although the OFT increases by approximately 3%, the friction force exceeds that of PLO at both dead-center and mid stroke. Under ASO-10 conditions, despite an average increase of approximately 15% in OFT, the friction force trend merely approaches or slightly matches that of PLO. As for ASO-25 condition, an increase in MOFT of up to 20% is required to maintain friction levels comparable to PLO, whereas the friction force increases sharply by nearly 30% when OFT differences diminish within the 90–180°CA interval. In contrast, the PAS condition remains within boundary lubrication, the reduction in friction force may be attributed to the unique lubrication behavior induced by tribochemical reactions.

3.3.2 Wear debris of lubricating oils

To further investigate the microscopic wear mechanisms under different lubrication conditions, residual oil samples were collected for ferrographic analysis. As shown in Figure 12, reflected light images of wear debris and corresponding size distribution statistics are presented. Wear severity and failure modes can be inferred from particle morphology and the proportion of abnormal particle sizes. Under PLO conditions, only mild wear is observed, characterized by low particle density and sparse distribution. The particles mainly consisted of regular lamellar and fine rubbing wear particles. Statistical results exhibit the lowest particle count across all conditions, with conventional particles ($<40\text{ }\mu\text{m}$) accounting for approximately 90%, while harmful abnormal particles ($>60\text{ }\mu\text{m}$) remain negligible, indicating a stable regime of normal rubbing wear [30].

Following ammonia gas contamination, a slight deterioration in wear behavior is observed in AGO. The particle density increases, accompanied by the emergence of occasional large chunk fatigue spall particles and spherical particles. Statistical analysis reveals that the wear severity becomes dependent on operating conditions. Particle density remains comparable to PLO at high speeds, while both conventional ($<40\text{ }\mu\text{m}$) and medium-sized ($40\text{--}60\text{ }\mu\text{m}$) particles increase significantly at low speeds [31]. Particularly under high load (600 N), even an increase in rotational speed fails to suppress accelerated particle generation. These observations suggest that contamination reduces load-bearing capacity of the oil film, promoting the evolution of wear behavior toward a combination of moderate sliding wear and mild fatigue wear.

In contrast, the introduction of ammonia solution (ASO) leads to a pronounced deterioration in wear state. Particle density increases significantly and forms coarse vertical accumulations, accompanied by the emergence of abnormal morphologies and corrosion particles exhibiting interference colors. Statistical results indicate extremely severe wear under both ammonia solution concentrations, with particle generation

increasing nonlinearly with load. Abnormal particles ($>40\ \mu\text{m}$) are exceedingly twice the number of PLO, indicating that the tribological pair has entered a stage of severe material delamination.

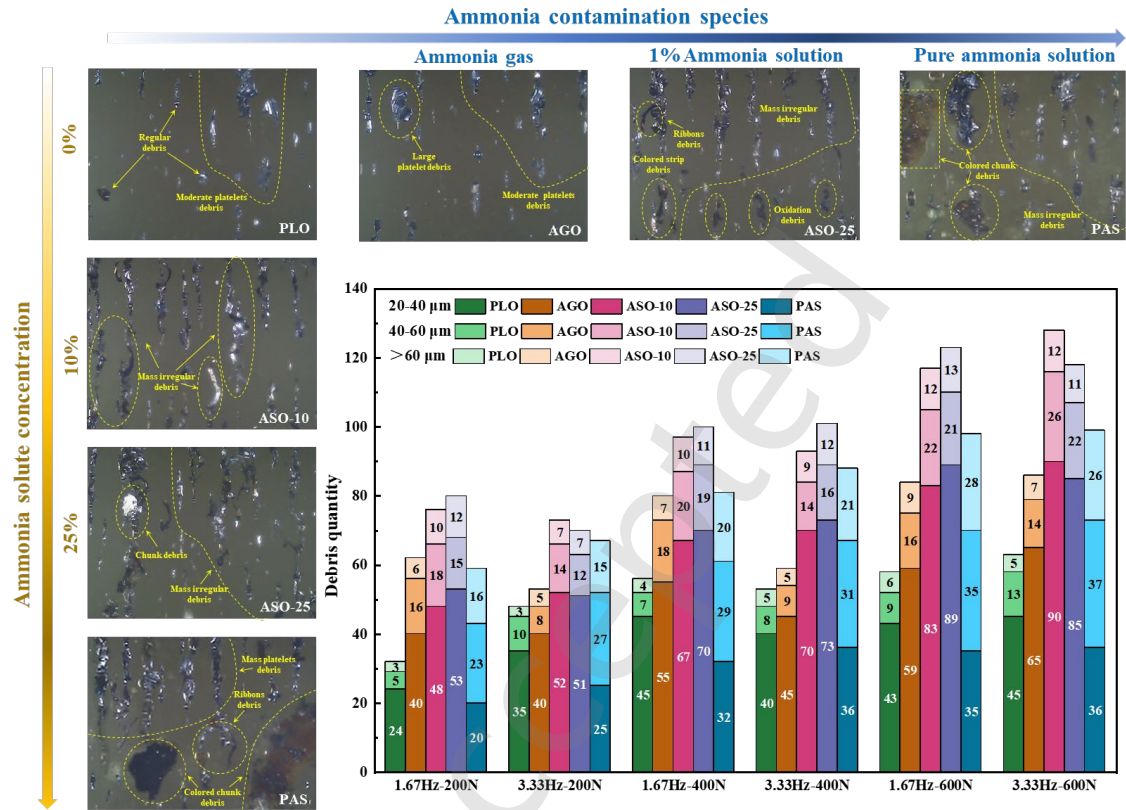


Figure 12 Ferrographic images and particle numbers of wear particles in lubricating oil under different contamination forms and ammonia concentrations at 1.67 Hz-600 N

With increasing concentration of ammonia solute, changes in particle morphology reflect the evolution of wear mechanisms. Under ASO-10 condition, numerous ribbon-like cutting particles with curled morphologies are observed, along with medium-sized flattened sliding particles exhibiting dull surfaces or typical oxidative particles with interference colors, indicating the occurrence of tribochemical reactions [32]. Therefore, the frictional interface is primarily characterized by a combination of moderate sliding wear, cutting wear, and pronounced oxidative wear. As for ASO-25 condition, large chunk fatigue spall particles with metallic luster appear, along with dense ribbon or strip-like cutting particles characterized by darkened and rough edges. Dense clusters of amorphous dark corrosive/oxidative particles are also observed surrounding primary debris, suggesting that the frictional interface evolves toward a synergistic combination of cutting wear, contact fatigue, and corrosive-wear.

Under the extreme PAS condition, characteristics of wear particles differ markedly from oil-lubricated systems. The density of large irregular, colored spherical and ribbon-

like particles increases significantly, accompanied by numerous non-metallic luster debris with surface discoloration. Additionally, widespread flocculent amorphous corrosion products are observed in the background, characterized by reddish-brown and yellowish-brown semi-transparent appearances. Statistical analysis indicates a reduction in total particle count compared with ASO conditions, while the proportion of harmful particles ($>60\text{ }\mu\text{m}$) is dominant, indicating severe abnormal wear. Considering that a thick passivation layer may form in ammonia solution, these low-strength corrosion layers undergo repeated spalling under shear stress [33]. Ultimately, the damage mechanism transitions into a severe corrosive–wear effect.

3.4 Vibration characteristics of CL-PRs

To investigate the vibration characteristics induced by friction behavior, a signal segment of approximately 2.2 s at 7000 s was selected for analysis. The ambient vibration acceleration amplitude ranged from -15 to 15 m/s^2 . This interval corresponds to the stable friction phase in 7 complete strokes and effectively captures the vibration response under different lubrication conditions. Subsequently, short-time Fourier transform (STFT) was applied to perform time-frequency analysis. The resulting spectrograms are expressed in terms of linear amplitude (m/s^2), with the amplitude normalization based on the maximum value further conducted to enhance contrast among characteristic frequency bands.

Figure 13 presents the time-domain vibration signals under various lubrication conditions. Under the no-load (Blank) condition, background noise remains extremely low, effectively excluding the influence of external excitation on the friction process. In comparison across conditions, PLO exhibits the lowest overall amplitude, characterized by continuous and uniform high-frequency micro-fluctuations, without any evident transient impact pulses, indicating a stable friction behavior. Under the AGO condition, although the baseline amplitude remains low, periodic discrete impact pulses begin to appear near the dead center, suggesting the onset of localized contact instability. Under ASO conditions, the baseline amplitude becomes noticeably broadened compared to AGO, with impact pulses occurring more frequently and in an irregular manner. The pulse width also increases, exhibiting typical excitation characteristics associated with rough surface contact. Notably, under ASO-25 conditions, the expansion of the baseline amplitude becomes pronounced, and the signal envelope shows a continuous widening trend, indicating further deterioration in surface roughness and contact stability. In contrast, although the PAS condition corresponds to the most severe surface damage, both the baseline amplitude and peak values decrease significantly, approaching the PLO levels. However, the signal becomes markedly irregular, with periodic reversal impact

features nearly disappearing.

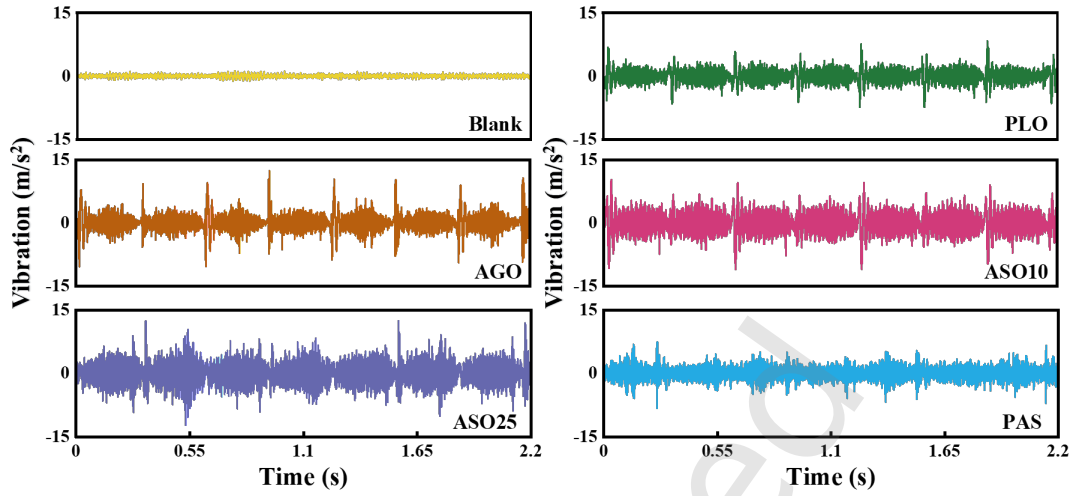


Figure 13 Time-domain frictional vibration signals under different lubrication conditions

Figure 14 presents the STFT time-frequency representations under different lubrication environments, along with the corresponding maximum amplitude and root mean square (RMS) values. The amplitude serves as a sensitive indicator of transient wear events such as material spalling and mechanical impacts, whereas the RMS more effectively characterizes sustained rough contact and cutting interactions.

A strong correspondence is observed between the time-frequency distribution and the time-domain characteristics, while a stable narrowband enhancement appears near approximately 4 kHz, which is presumed to be associated with inherent structural responses or background resonance. Under the PLO condition, energy distribution remains uniform throughout the frequency range and at an overall low level, with energy predominantly concentrated below 1 kHz. Correspondingly, as shown in Figure 14(b), both maximum amplitude and RMS maintain the lowest baseline values, reflecting a stable sliding friction. With the introduction of ammonia contamination, high-energy regions progressively expand toward broader frequency ranges, accompanied by an overall increase in background energy, which drives a stepwise rise in both amplitude and RMS. Under the AGO condition, periodic impact bands are distributed at equal intervals along the time axis, corresponding to impact events in the reversal region. Under the ASO-10 condition, a significant increase in background vibration energy is evident, while vertical impact bands extend toward higher frequencies and span a wider frequency range, leading to a pronounced increase in RMS. This indicates intensified rough contact and asperity interaction in addition to impact events.

The energy distribution under ASO-25 is generally similar to ASO-10, whereas a broader spread and stronger accumulation of energy are observed in the low-frequency

region below 2 kHz. Meanwhile, periodic impact bands become denser and more intense, extending across nearly the entire frequency range of 0-5 kHz. Compared with PLO, the amplitude and RMS increase by 48.5% and 101%, respectively. Under the PAS condition, the overall energy density decreases noticeably and becomes more uniformly distributed, while high-frequency impact bands are substantially weakened. Both amplitude and RMS approach the PLO levels, while energy becomes concentrated in the low-frequency region around 500 Hz. Additionally, several horizontal high-energy lines appear within the 3.5-5 kHz range, which are likely associated with continuous mechanical contact and friction-induced noise caused by dry friction.

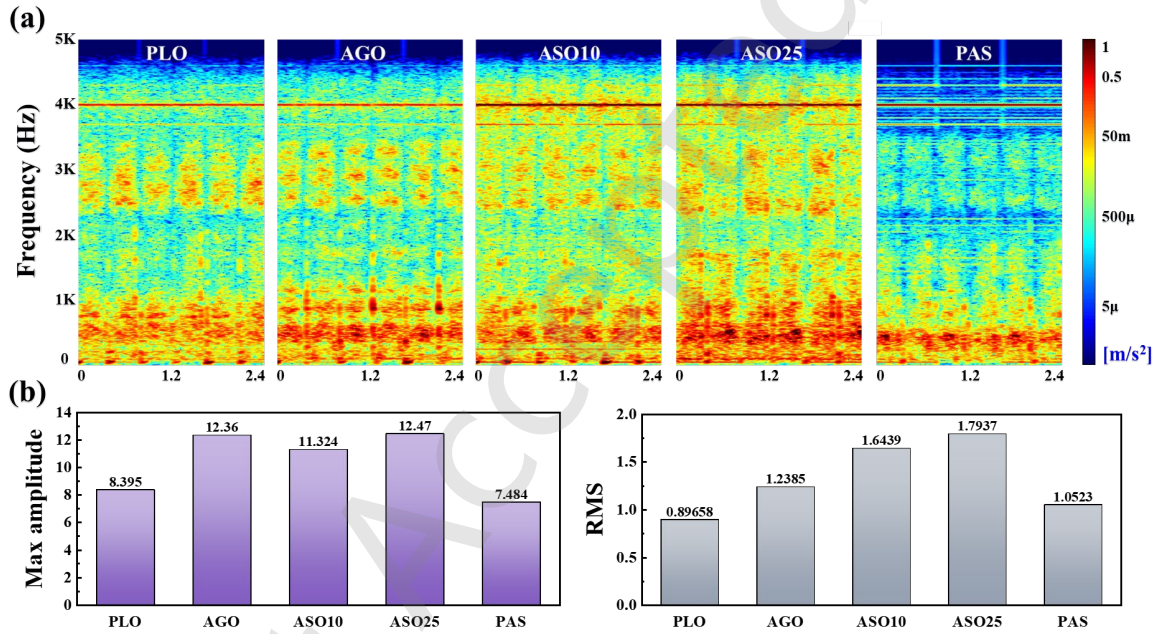


Figure 14 (a) STFT time–frequency maps and (b) corresponding maximum amplitude and RMS of vibration signals under different lubrication conditions

4 Discussion

This study systematically investigates the tribological performance of the CL-PR system under multiple representative lubrication environments in ammonia engines, thereby revealing the influence mechanism of the introduction form and concentration of ammonia contamination on friction and wear behavior. Experimental results demonstrate that the introduction form of ammonia contaminants is closely associated with the transition of interfacial damage from mechanical wear to corrosion-wear effects, while increasing contamination degree primarily dictates the severity and depth of damage.

Specifically, the introduction of ammonia contaminants significantly deteriorates the lubrication performance of CL-PR friction pair by altering the rheological behavior of the lubricant. Previous studies have revealed that ammonia gas reacts with additive

components to form complexes, while ammonia solution induces severe emulsification and precipitation, leading to a marked increase in oil viscosity [14]. Although this may lead to an apparent increase in OFT, the presence of multiphase contaminants impairs the mobility, continuity, and replenishment capacity of the lubricant, thereby offsetting the lubrication enhancement associated with increased OFT. In this context, PLO achieves superior lubrication and surface separation despite a lower apparent OFT, owing to its ideal continuity, uniformity, and rheological resilience. Whereas for AGO conditions, lubricant degradation is primarily reflected in the weakening of film continuity and local starvation, especially near dead-center regions. However, the complexes tend to dissociate under frictional heating and lead to a rapid reduction in oil viscosity and partial recovery of flowability and shear response, allowing the COF to approach PLO levels under severe conditions and maintaining moderate film strength within the sliding regions.

In comparison, the synergistic interaction between ammonia and water in ASO conditions promotes the formation of emulsified dispersed phases under shear, accompanied by localized cavitation and oil-air mixture [34]. Meanwhile, the reduced capacity of lubricant replenishment promotes frequent film rupture within the contact region, resulting in a lubrication regime dominated by starvation despite apparently elevated OFT levels. Furthermore, the lubrication behavior under PAS conditions differs fundamentally from that of oil-lubricated systems, where the negligible load-carrying capacity of the aqueous medium leads to severe boundary lubrication and asperity contact, resulting in an extremely high COF and material removal. However, the chemical reactivity of PAS promotes tribochemical reactions under frictional heating, potentially forming product layers that provide solid lubrication and lead to an anomalous reduction in COF at elevated loads.

Moreover, ammonia contamination led to a pronounced degradation of the anti-wear performance of lubricating oil through additive depletion and interfacial deterioration by chemical activity. In the absence of contamination, calcium-based detergents exhibit excellent anti-wear performance, as evidenced by the elemental distribution in Figure 10 and the XPS spectra in Figure 15, where a tribofilm with relatively high hardness and shear strength is formed, thereby effectively facilitating interfacial separation and load transfer [35,36], resulting in a smooth worn surface and the lowest wear rate.

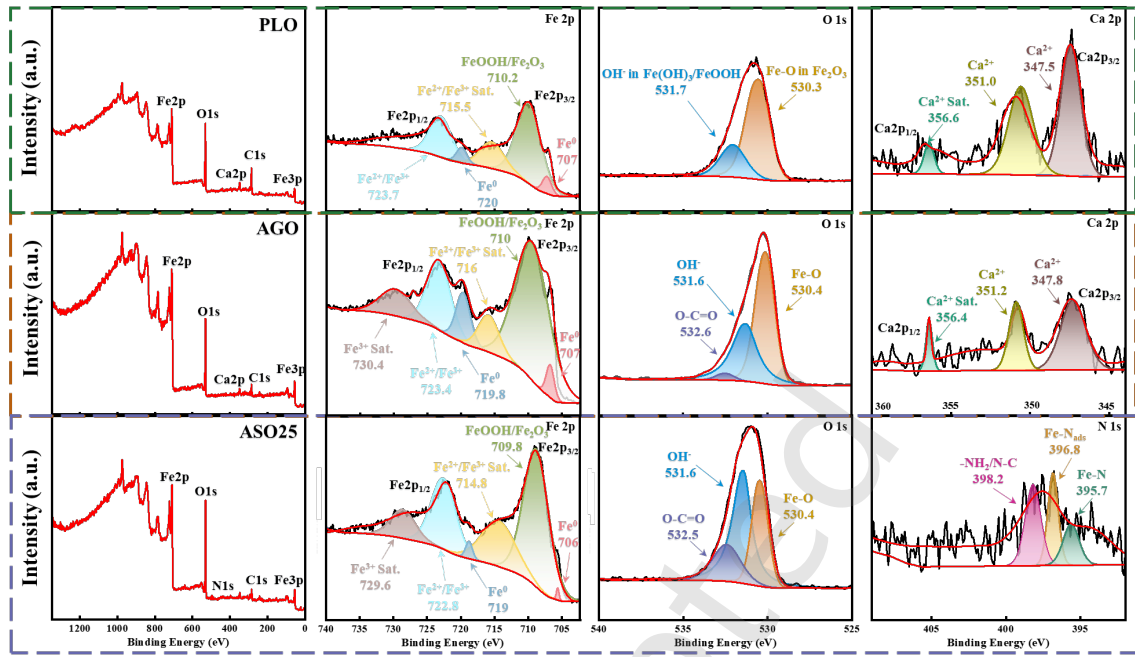


Figure 15 XPS spectra of worn liner surfaces in regions of Fe 2p, O 1s, Ca 2p and N 1s under different lubrication conditions

Under AGO conditions, the complex reaction will lead to additive partial depletion and micellar dispersion disruption, resulting in a reduction in the coverage and integrity of the tribofilm, as evidenced by the decreased calcium content and peak intensity in the corresponding XPS spectra. Therefore, enhanced mechanical contact and substrate exposure promote friction oxidation, resulting in the formation of iron oxide layers. This is further supported by a reduction of approximately 10% in hardness and elastic modulus of the worn surface compared with PLO, as shown in Figure 16, since the oxide-derived layer is mechanically inferior to the calcium-based tribofilm [37]. The combined effect of weakened interfacial strength and increased mechanical contact due to reduced oil film strength promotes the formation of larger wear debris, which may undergo repeated rolling and plastic deformation within the contact zone and present the morphology characteristics shown in Figure 12. Concurrently, deeper ploughing grooves, layered structures, and micro-cracks are observed on the worn surface. These features indicate that the wear mechanism evolves toward mild adhesive wear, fatigue cracking, and oxidative wear, although mechanical damage remains the primary mode.

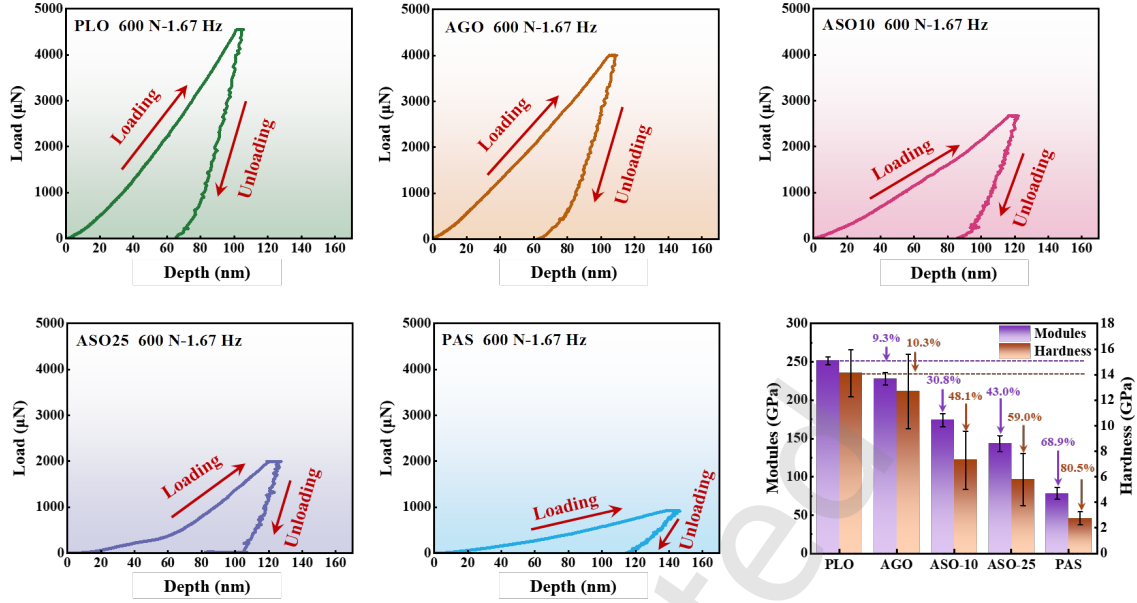


Figure 16 Load-displacement curve, Young's modulus and hardness of liner surface under different lubrication conditions

Further deterioration of anti-wear performance is observed when ammonia solution is introduced (ASO), where the synergistic effects of moisture and active ions fundamentally alter the nature of interfacial damage. Lubrication degradation and chemical activity become dominant, as additives are consumed through emulsification, precipitation, and hydrolysis, leading to failure of calcium-based tribofilms and enhanced corrosion damage. Consequently, while lubrication performance deteriorates and physical damage is intensified, an aggressive chemical damage mechanism is simultaneously introduced. At low ammonia concentrations (ASO-10), hydroxyl ions produced by the dissociation of ammonia solution will promote additive hydrolysis and participate in tribochemical reactions, thereby partially dissolving the substrate and accelerating the formation of corrosion products, which is reflected by oxygen and copper enrichment in Figure 10. The alteration of mechanical properties further reveals that the elastic modulus and hardness of the worn surface decrease by more than 30% compared with PLO condition, indicating that interfacial degradation transitions toward surface softening and spalling induced by corrosion effect, with the load-bearing structure evolving from a dense and stable framework to a loose product layer.

As a result, these layers become susceptible to collapse, cracking, and repeated delamination under cyclic shear stress, leading to abnormal damage. Accordingly, elongated ribbon-like cutting debris and discolored corrosive debris are observed to increase in Figure 12, while the worn surface exhibits deeper and wider ploughing grooves, localized spalling, and micro-pitting. These characteristics suggest that the

dominant damage mechanism shifts from mechanical wear to tribocorrosion, characterized by a coupled effect of moderate fatigue wear, abrasive wear, and pronounced oxidative wear.

With further increases in ammonia concentration (ASO-25), the synergistic action of abundant ammonium species, hydroxyl ions, and water accelerates additive hydrolysis and precipitation, leading to almost failure of the protective tribofilm and a substantial intensification of tribochemical reactions. In this context, the flash temperatures may further promote nitriding reactions at active sites, leading to the formation of Fe–N compounds, accompanied by possible amination or condensation reactions generating nitrogen-containing aggregates [38]. In parallel, oxidation and hydroxylation processes at the friction interface become intensified, promoting a transition of corrosion products from relatively dense Fe_2O_3 to predominantly porous FeOOH structures [39]. Corresponding evidence is provided by the peak intensities shown in Figure 15 and the mechanical properties in Figure 16, where reductions in elastic modulus and hardness reach 43% and 59% respectively compared with PLO. This implies that increasing ammonia concentration accelerates interfacial weakening and promotes deeper corrosion penetration, resulting in extensive subsurface defects and undermining the load-bearing structure. As a result, a thickened corrosion layer with low bonding strength and limited yield resistance is formed.

Subsequently, corrosive species penetrate preferentially along internal weak regions, inducing deep substrate degradation and pitting formation. During continued frictional processes, the extensive but structurally loose corrosion layer experiences progressive damage and repeated delamination, thereby triggering severe material removal and exposure of the graphite phase. Consequently, dense micro-pits, accumulated corrosion products, and dispersed brittle nitrides function as stress concentrators or third-body abrasives, promoting the macro ploughing grooves, large-scale spalling, and fatigue crack propagation shown in Figure 8. The resulting wear debris primarily consists of discolored particles with pronounced corrosion characteristics and irregular morphologies, indicating that severe contact fatigue, delamination wear, and abrasive wear driven by corrosive–wear coupling effect have become the primary failure modes. Furthermore, PAS can be regarded as a reference representing an extreme environment, where a low-strength and porous passive film will rapidly form on the substrate due to strong alkalinity, while undergoing cyclic delamination and regeneration under friction shear, leading to a markedly elevated wear rate [40]. As illustrated in Figure 8, large-scale corrosion regions characterized by a rough, sponge-like morphology are observed, indicating that the wear

process is likely dominated by tribochemical reactions and involves severe corrosion-wear synergistic damage.

Finally, ammonia contamination will further deteriorate the vibration behavior of CL-PR friction pair, with dynamic response closely correlating with lubrication degradation and interfacial damage evolution. Under PLO conditions, the ideal strength and continuity of oil film provide sufficient fluid damping to absorb vibrations. The tribofilm with high shear strength and hardness provides extensive coverage, which effectively isolates mechanical contact even in the mixed lubrication range, playing an effective role in cushioning vibrations [41]. Under the AGO condition, reduced lubrication effectiveness in the reversal zone leads to an increase in vibration amplitude and energy distribution within the impact region, whereas the oil film in the sliding region retains adequate bearing capacity, no extensive surface defects have developed, and the remaining tribofilm continues to provide partial protection. As a result, the RMS values and background energy distribution of the vibration signals remain comparable to those under the PLO condition.

With further contamination of ASO, the expansion of starved contact regions promotes more frequent mechanical contact, while surface structural defects and corrosion layers intensify rough contact and asperity interactions during friction. Accordingly, irregular impact peaks emerge in the vibration signals within the sliding region, accompanied by a significant increase in RMS values [42]. Considering the correlation between vibration characteristics and wear states, these observations further indicate that higher concentrations of ammonia solute correspond to more severe lubrication degradation and interfacial deterioration. As for PAS condition, the presence of a corrosion product layer may provide solid lubrication and damping, leading to a transition of the vibration response from high-frequency rigid behavior to low-frequency stick-slip and delamination behavior, thereby shifting the dominant response frequency below that of metallic contact [43].

In summary, the deterioration of CL-PR tribological performance under ammonia contamination can be attributed to the coupled effects of lubrication degradation and interfacial tribochemical deterioration. Ammonia contamination alters rheological properties of lubricating oil through emulsification, flocculation, and precipitation, thereby weakening the continuity, replenishment, and load-carrying capacity of oil film. Moreover, interactions among contaminants, degraded additives, and the metal surface weaken tribofilms and promote the formation of Fe_2O_3 / FeOOH corrosion layers or nitrogen reactant. Specifically, contamination by ammonia gas primarily accelerates

degradation of both oil film and tribofilm, thereby intensifying mechanical wear. In contrast, contamination by ammonia solution further introduces chemical degradation of the friction surface, rendering it more susceptible to corrosive-wear. With increasing concentration of ammonia solute, both lubrication degradation and interfacial damage become more pronounced, the expansion of starved regions elevates the susceptibility to chemical corrosion and nitriding reactions within the contact zone. As pitting intensifies and corrosion layers grow increasingly thick and fragile, surface damage is more likely to extend into the subsurface, ultimately accelerating fatigue spalling and abrasive wear. The influence mechanisms of ammonia contamination on CL-PR friction pairs are summarized in Figure 17.

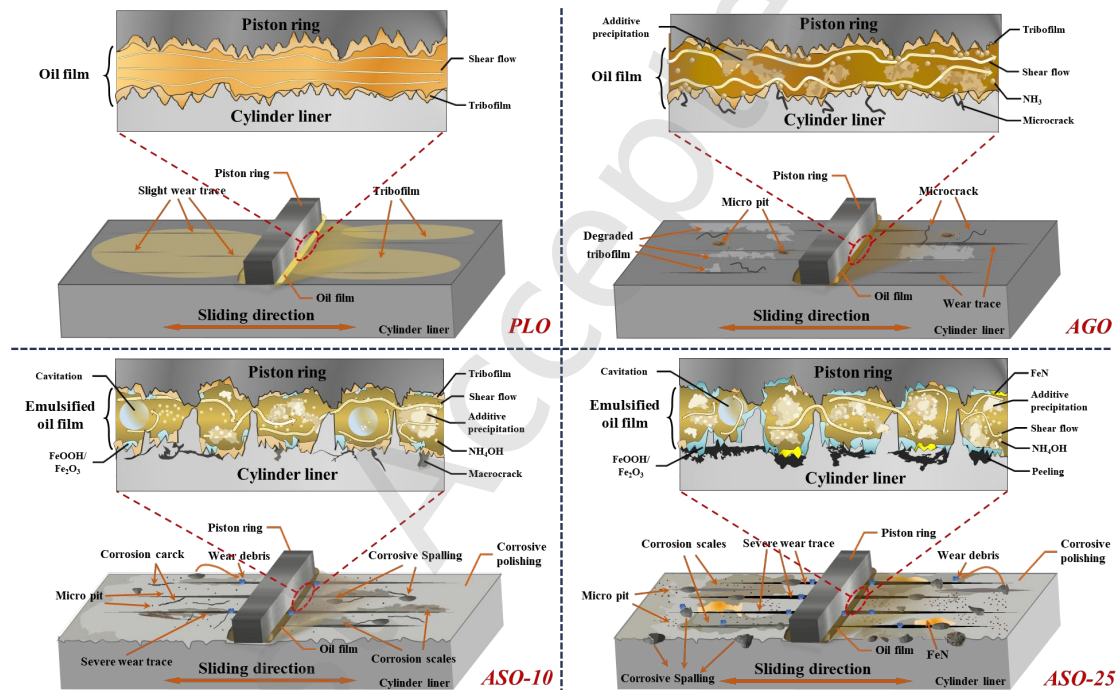


Figure 17 Diagram of tribological performance degradation mechanism of CL-PR under different lubrication conditions

5 Conclusions

In this study, the tribological performance of CL-PR under ammonia-contaminated lubrication conditions was systematically investigated by simulating realistic service conditions in ammonia engines. A series of lubrication media were prepared by controlling the form and concentrations of ammonia contamination, and the friction coefficient, oil film thickness, vibration dynamic response, wear rate, and microscopic wear morphology of CL-PR were comprehensively analyzed. Furthermore, by combining surface chemical distribution with mechanical properties, the potential mechanism of tribological degradation driven by ammonia contamination was explored. The main

conclusions are summarized as follows:

(1) Ammonia contamination universally leads to deterioration in the tribological performance of the CL-PR system, with the extent of degradation strongly dependent on both contamination form and ammonia concentration. Compared with ammonia gas, ammonia solution exerts pronounced adverse effect on the interface, which intensifies with increasing ammonia concentration.

(2) The introduction of ammonia contaminants will severely degrade lubrication performance of the lubricant. Both gaseous and aqueous ammonia contamination are associated with an apparent increase in OFT, whereas the integrity and replenishment capacity of the oil film are significantly impaired, rendering the contact interface susceptible to localized starvation, leading to abnormal increases in friction and vibration.

(3) The introduction form of contaminant governs the evolution of tribochemical reactions and product formation. Ammonia gas contamination primarily reduces the coverage of tribofilms, exposing the substrate and intensifying tribo-oxidation, resulting in the formation of thin oxide layers and oxygen-containing organic compounds. In contrast, ammonia solution contamination promotes interfacial activation and accumulation of corrosion products, forming a reaction layer dominated by oxidation/hydroxylation products. With increasing ammonia concentration, the critical oxide transitions from dense Fe_2O_3 to porous FeOOH structure, accompanied by potential localized nitriding reactions and Cu enrichment, ultimately leading to significant degradation of the load-carrying capacity.

(4) Ammonia gas contamination mainly weakens anti-wear performance of additives and intensifies mechanical contact, driving interfacial damage toward mild abrasive wear, oxidative wear, and fatigue spalling. In contrast, ammonia solution contamination further induces corrosion, surface softening, pitting, and crack propagation, increasing abnormal wear debris, wear rate, and delamination severity. As ammonia concentration increases, corrosion damage extends from the surface to deeper substrate, and the friction interface exhibits pronounced corrosive-wear and fatigue spalling characteristics.

In conclusion, the present investigation provides valuable insights into the degradation pathways and damage mechanisms of CL-PR friction pairs within ammonia engines, and also establishes a foundation for preventing abnormal damage and corrosive-wear. Future work will focus on the temperature variations during engine operation to further elucidate the temperature-dependent evolution of tribological performance degradation.

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Declaration of Interest Statement

The authors have no competing interests to declare that are relevant to the content of this article.

Data availability statement

Raw data will be made available upon request.

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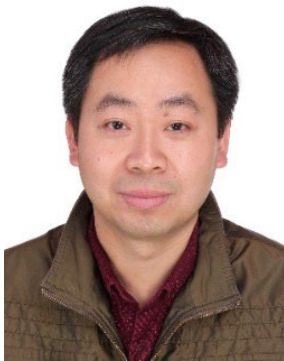


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