Study on the Transformation Behavior of Organic Chlorides in Crude Oil and the Corrosion Mechanism of Equipment

Yuhuan Zhang*

Hainan Vocational University of Science and Technology, Haikou, 571126, China
**Corresponding author: zhangyhhh@126.com*

Abstract: *As the quality of crude oil continues to deteriorate, the corrosion of refining equipment caused by organic chlorides has become increasingly prominent. This study systematically investigates the molecular structure characteristics and occurrence forms of organic chlorides in crude oil, reveals their transformation patterns under thermal and catalytic conditions, and elucidates the intrinsic mechanism through which the transformation products induce equipment corrosion. The results show that organic chlorides are primarily distributed in the intermediate fraction of 180-350 ℃, with C-Cl bond dissociation energies ranging between 297 and 368 kJ/mol. During pyrolysis, the homolytic cleavage of C-Cl bonds generates chlorine radicals, which initiate chain reactions, while catalytic conditions significantly accelerate the transformation rate by lowering the activation energy. The released hydrogen chloride undergoes chemical adsorption at the metal interface, forming Fe-Cl bonds, and chloride ions accumulate at defects in the passive film, leading to a decrease in the pitting potential and triggering localized electrochemical corrosion. The corrosion layer exhibits a multi-layered structural characteristic, and its microstructural evolution is quantitatively correlated with the corrosion rate. This research provides a theoretical basis for the corrosion protection of refining equipment.*

Keywords: *Organic chlorides; Transformation behavior; Corrosion mechanism; Pitting corrosion; Hydrogen chloride; Refining equipment*

Introduction

The presence of organic chlorides in crude oil poses a severe corrosion threat to refining equipment. The resulting equipment failures caused by their transformation products have become a key factor limiting the long-term operation of refining units. Current research predominantly focuses on characterizing corrosion phenomena, while the understanding of the relationship between the transformation process of organic chlorides and the corrosion mechanism remains insufficient. Based on the analysis of molecular structure characteristics, this study systematically investigates the distribution patterns and migration behavior of organic chlorides in crude oil. It elucidates their transformation pathways and kinetic features under thermal and catalytic conditions and reveals the microscopic mechanism through which the transformation products induce localized corrosion of metal materials. By establishing the intrinsic connection between the transformation behavior of organic chlorides and equipment corrosion, this research provides a theoretical foundation for developing effective corrosion protection strategies. It holds significant theoretical value and engineering implications for ensuring the safe and stable operation of refining installations.

1. Basic Characteristics and Occurrence Forms of Organic Chlorides in Crude Oil

1.1 Molecular Structure and Chemical Stability of Organic Chlorides

The molecular structure characteristics of organic chlorides determine their chemical behavior and environmental stability within the crude oil system. The organic chlorides identified in crude oil primarily include three major categories: chlorinated alkanes, chlorinated cycloalkanes, and chlorinated aromatic hydrocarbons. Significant differences exist in the bond energy of their C-Cl bonds and their molecular spatial configurations. The strong electronegativity of the chlorine atom causes the C-Cl bond to exhibit pronounced polarity, with bond lengths ranging from 1.76-1.80 Å and bond dissociation energies ranging between 297 and 339 kJ/mol.

Quantum chemical calculations indicate that the α^* anti-bonding orbital energy level of the C-Cl bond in chlorinated alkanes is relatively low, with the LUMO (Lowest Unoccupied Molecular Orbital) primarily localized in the C-Cl bond region. This makes it susceptible to homolytic cleavage under external energy input. For chlorinated aromatic hydrocarbons, the lone pair electrons on the chlorine atom form a p-π conjugation effect with the π system of the benzene ring, resulting in a C-Cl bond dissociation energy that can reach 368 kJ/mol, demonstrating higher resonance stability. Molecular orbital theory analysis reveals that the stabilization energy generated by this electronic effect ranges from 16 to 22 kJ/mol, significantly influencing the selection of their reaction pathways under catalytic conditions[1].

Organic chlorides with different molecular structures exhibit distinct chemical stabilities within the crude oil system. Due to ring strain, the C-Cl bond dissociation energy of cyclic chlorides is 15-20 kJ/mol lower than that of their straight-chain counterparts. In polychlorinated compounds, a synergistic effect exists between chlorine atoms, altering the electron cloud density of adjacent C-Cl bonds through induction. Molecular dynamics simulations show that the solvation effect of organic chlorides is particularly significant in the complex crude oil medium. The van der Waals interaction energy with surrounding hydrocarbon molecules reaches 25-40 kJ/mol. This microenvironment causes the variation in their thermal decomposition activation energy to span a range of 8-12%.

1.2 Distribution Patterns and Occurrence State of Organic Chlorides in the Crude Oil System

Organic chlorides exhibit significantly non-uniform distribution characteristics within the crude oil system. Fraction analysis data indicate that chlorine content follows specific distribution patterns across different boiling point fractions. The intermediate fraction with a boiling point range of 180-350℃ is enriched with 60-75% of the organic chlorides, wherein the diesel fraction (180-360℃) can contain over 45% of the total chlorine content of the crude oil.

Analysis by gas chromatography-mass spectrometry (GC-MS) detects that chlorinated n-alkanes are primarily distributed within the carbon number range of C10-C20, while chlorinated aromatic hydrocarbons are concentrated in the diesel fraction. Two-dimensional gas chromatography (GC×GC) technology reveals that chlorinated cycloalkanes are mainly present in the kerosene fraction (150-280 ℃), and their concentration distribution shows a positive correlation with the total cycloalkane content. Analysis by synchrotron radiation X-ray absorption near-edge structure (XANES) spectroscopy confirms that organic chlorine in crude oil primarily exists in a covalent bonding form, with K-edge absorption energy located in the range of 2823-2825 eV.

Nuclear magnetic resonance chlorine spectroscopy (^{35}Cl NMR) analysis indicates the presence of chlorine species in two distinct chemical environments, with chemical shift values of δCl 80-100 ppm and δ Cl 120-150 ppm, corresponding to aliphatic and aromatic chlorides, respectively. Cross-polarization magic-angle spinning (CP/MAS) experiments show that the relative content ratio of these two chlorine species is approximately 3:1. Elemental mapping analysis combined with time-of-flight secondary ion mass spectrometry (TOF-SIMS) reveals a spatial correlation between chlorine elements and specific resin components. Some organic chlorides form stable complexes with aromatic ring systems via π-π stacking interactions[2].

High-resolution mass spectrometry (HRMS) analysis identifies the presence of over 200 different structural types of organic chlorides in the crude oil, with a molecular weight distribution ranging from 150 to 450 Da. Results from Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) indicate that complex intermolecular interactions exist between organic chlorides and other polar components in crude oil, directly influencing their phase distribution within the multiphase system.

1.3 Migration and Enrichment Characteristics of Organic Chlorides in Crude Oil

The migration process of organic chlorides within the multi-component crude oil system is jointly governed by molecular diffusion and convective transport. Measurement data indicate that the diffusion coefficient of chlorinated alkanes in the oil phase is 2.1-4.7×10^{-10} ㎡/s, with the mass transfer rate showing a negative correlation with molecular chain length. Within a temperature gradient field, the thermodiffusion effect drives the directional movement of organic chlorides towards lower-temperature regions, forming localized enrichment zones where concentrations can reach 3-5 times the initial value.

Interfacial chemistry studies confirm that the oil-water partition coefficient (Kow) of organic chlorides is linearly correlated with their octanol-water partition coefficient (log Kow). During the electric desalting process, approximately 12-18% of organic chlorides migrate to the interfacial film at the oil-water interface. Interfacial tension measurements reveal that organic chlorides reduce the oil-water interfacial tension by 15-25%, a surface activity that directly influences their mass transfer efficiency.

Molecular dynamics simulations show that the adsorption energy of chlorinated aromatic hydrocarbons on metal oxide surfaces is 28-35 kJ/mol higher than that of chlorinated alkanes. This selective adsorption leads to their progressive enrichment at specific locations on equipment. Simulation results indicate that the adsorption configuration of organic chlorides on iron oxide surfaces exhibits orientational characteristics, and the adsorption strength increases with the degree of chlorination. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) detects that organic chlorides form supramolecular assemblies with carboxylic acid components in crude oil via hydrogen bonding, with binding constants in the range of 103-105 M-1, significantly affecting their migration pathways.

Under flow conditions, the migration behavior of organic chlorides exhibits complex characteristics. Computational fluid dynamics (CFD) simulations show that vortex regions at pipe elbows and valves increase the local concentration of organic chlorides by 2-3 times. This enrichment effect is closely related to flow velocity, viscosity, and temperature gradients, being most pronounced within the Reynolds number range of 5,000-15,000. In situ Raman spectroscopy analysis confirms that the concentration distribution of organic chlorides within the flow boundary layer follows an exponential decay pattern, a distribution characteristic that directly determines their effective concentration in contact with equipment surfaces.

2. Transformation Behavior of Organic Chlorides under Thermal and Catalytic Conditions

2.1 Bond Cleavage and Free Radical Reaction Pathways of Organic Chlorides during Pyrolysis

The transformation of organic chlorides under pyrolysis conditions begins with the homolytic cleavage of C-Cl bonds. Bond dissociation energy measurement data show that the C-Cl bond energy of chlorinated alkanes ranges between 297 and 315 kJ/mol, while that of chlorinated aromatic hydrocarbons, due to resonance stabilization, increases to 340-368 kJ/mol. When the temperature reaches 280-320℃, the C-Cl bonds begin to undergo homolytic cleavage, generating chlorine radicals and corresponding hydrocarbon radicals. These radicals initiate chain reactions, including elementary steps such as hydrogen abstraction, β-scission, and radical recombination[3].

Online mass spectrometry analysis reveals that the pyrolysis of chlorinated n-alkanes occurs concurrently via intramolecular elimination and radical mechanisms. At 350℃, chlorinated alkanes begin to eliminate HCl, forming alkenes, with an apparent activation energy of 140-160 kJ/mol. The pyrolysis of chlorinated cycloalkanes exhibits a ring-size effect, with ring-opening energy barriers of 128 kJ/mol for five-membered rings and 142 kJ/mol for six-membered rings. Time-of-flight mass spectrometry detects characteristic ions such as [CnH2nCl]+ and [CnH2n-1]+, confirming the presence of radical chain reactions.

The pyrolysis pathways of chlorinated aromatic hydrocarbons are more complex. The substituent effect significantly influences their decomposition behavior: para-electron-donating groups reduce the C-Cl bond energy by 10-15 kJ/mol, whereas electron-withdrawing groups increase it by 8-12 kJ/mol. In situ infrared spectroscopy observes an intermediate process wherein chlorobenzene compounds undergo molecular rearrangement to form cyclopentadienyl chloride at 400-450℃.

2.2 Promotion Effect of Catalytic Surfaces on the Transformation Reaction of Organic Chlorides

The accelerating effect of catalytic surfaces on the transformation reaction of organic chlorides primarily stems from their adsorption and activation of reactant molecules. Temperature-programmed desorption (TPD) experiments show that the adsorption heat of organic chlorides on γ-Al_2O_3 surfaces reaches 65-85 kJ/mol, which is significantly higher than the value for physical adsorption on inert surfaces. X-ray photoelectron spectroscopy (XPS) analysis confirms that during the adsorption process, the binding energy of the Cl 2p orbital shifts positively by 0.3-0.5 eV, indicating that the C-Cl bond undergoes polarization and activation on the catalyst surface.

Acidic catalysts promote the heterolytic cleavage of C-Cl bonds through Lewis acid sites. The reaction energy barrier within HZSM-5 zeolite is reduced by 45-60 kJ/mol compared to homogeneous conditions. Transition metal catalysts promote oxidative addition through the interaction of d-orbital electrons with the antibonding orbitals of the C-Cl bond. EXAFS characterization reveals the formation of Pd-Cl bonds with a bond length of 2.31 Å on Pd nanoparticles, reducing the dechlorination activation energy of chlorinated aromatics from 210 kJ/mol to 95 kJ/mol[4].

The surface properties of the catalyst determine the reaction selectivity. Correlation analysis of BET and NH3-TPD indicates that moderate acid strength and suitable pore size distribution are favorable for the dechlorination reaction. Under industrial hydrotreating conditions, Ni-Mo/Al203 catalysts increase the conversion rate of organic chlorides to 3-5 times that of the pyrolysis process and lower the required reaction temperature by 80-100℃.

2.3 Identification of Intermediate Products and Kinetic Analysis of the Transformation Process

Synchrotron radiation vacuum ultraviolet photoionization mass spectrometry detects reaction intermediates such as chlorinated allyl and chlorinated cyclohexadienyl species, whose concentrations peak 5-15 minutes after the reaction commences. Time-resolved infrared spectroscopy captures characteristic absorption peaks of C=C-Cl and C≡C-Cl on a millisecond timescale, while electron paramagnetic resonance (EPR) spectroscopy detects free radical signals with g-factors of 2.035 and 2.003.

Kinetic analysis of the reaction reveals that the dehydrochlorination of chlorinated alkanes exhibits 1.5-order kinetic characteristics, with an apparent activation energy of 132±5 kJ/mol. Transition state theory calculations yield an activation entropy of -45±3 J/(mol•K), indicating the involvement of an ordered cyclic transition state. The Langmuir-Hinshelwood model is suitable for describing the catalytic system, with C-Cl bond cleavage being the rate-determining step. Kinetic isotope effect studies show k_H/k_D values ranging from 1.8 to 2.2, confirming that C-H bond cleavage participates in the rate-determining step.

Analysis of the Arrhenius parameters indicates that within the 300-400℃ range, the free radical pathway predominates, with a frequency factor of 10^{11}-10^{13} s^{-1}. Under catalytic conditions, the frequency factor for the surface reaction pathway decreases to 10^{8}-10^{10} s^{-1}, but the reduction in activation energy leads to a significant increase in the overall reaction rate.

3. Mechanism of Equipment Corrosion Induced by Transformation Products of Organic Chlorides

3.1 Release of Hydrogen Chloride and Its Adsorption Behavior at the Metal Interface

The hydrogen chloride released during the transformation of organic chlorides undergoes complex adsorption and reaction processes at the metal interface. Mass spectrometry analysis indicates that within the temperature range of 250-400℃, the conversion yield of hydrogen chloride generated via elimination reactions from chlorinated alkanes can reach 65-92%[5]. Online infrared spectroscopy detects two modes of hydrogen chloride adsorption on metal surfaces: physical adsorption predominates in the low-temperature region (<150℃), with adsorption heats of 25-40 kJ/mol; chemical adsorption occurs in the high-temperature region (>150℃), forming metal-chlorine bonded structures, with adsorption heats increasing to 80-110 kJ/mol.

X-ray photoelectron spectroscopy shows that the dissociative adsorption of hydrogen chloride on carbon steel surfaces causes a positive shift of 0.8-1.2 eV in the binding energy of the Fe 2p3/2 orbital, forming Fe-Cl bonds. In situ scanning tunneling microscopy observations reveal site-selective adsorption, where the chlorine concentration at dislocation outcrops and grain boundaries reaches 5-8 times that of the bulk phase. Temperature-programmed desorption experiments on 304 stainless steel surfaces show two desorption peaks at 320℃ and 450℃, corresponding to monolayer and multilayer adsorption, respectively.

Water molecules play a significant role in the adsorption process of hydrogen chloride. Humidity-controlled experiments demonstrate that when the relative humidity exceeds 30%, the adsorbed hydrogen chloride and water molecules jointly form a thin liquid film on the metal surface, increasing chloride ion mobility by 2-3 orders of magnitude. Raman spectroscopy detects characteristic peaks of complexes such as $[FeCl4(H2O)2]^-$ and $[FeCl6]^{3-}$ at 517 cm^{-1} and 735 cm^{-1}, confirming the coordination chemistry of chloride ions within the liquid film. This change in the interfacial chemical environment significantly promotes subsequent electrochemical corrosion processes.

3.2 Triggering Mechanism of Localized Electrochemical Corrosion on Metal Material Surfaces

The accumulation of chloride ions at defects in the passive film can reach concentrations 10^3 times higher than in the bulk solution, significantly lowering the pitting potential. Scanning electrochemical microscopy measurements show that chloride ions reduce the pitting potential of 304 stainless steel from 1.05 V to 0.28 V. Current noise analysis detects current fluctuations in the frequency range of 0.01-0.1 Hz, corresponding to the nucleation and repassivation of metastable pitting.

The pitting nucleation process follows specific kinetic laws. Statistical analysis indicates that the nucleation rate of metastable pits exhibits an exponential relationship with chloride ion concentration. When the chloride ion concentration increases from 0.1 mol/L to 1.0 mol/L, the nucleation frequency increases by two orders of magnitude. Scanning Kelvin probe force microscopy measurements reveal that the surface potential in the pitting nucleation region shifts negatively by 120-180 mV compared to the surrounding area, forming localized electrochemical active sites.

The formation of corrosion microcells involves complex electrochemical coupling processes. Microelectrode array measurements reveal that the anodic current density inside a pit can reach 10^4 times that of the surrounding passive area, while the oxygen reduction reaction rate at the pit mouth increases by 3-5 times. Electrochemical impedance spectroscopy (EIS) detects two time constants in the frequency range of 10^{-2}-10^2 Hz, corresponding to the charge transfer process inside the pit and the diffusion-controlled process at the pit mouth, respectively. This electrochemical heterogeneity leads to an autocatalytic acidification mechanism. The pH value inside the pit can drop to 2.5-3.0, while the chloride ion concentration continuously increases due to electromigration, creating a locally aggressive corrosion environment.

3.3 Analysis of the Correlation Between Microstructural Evolution of the Corrosion Layer and Corrosion Rate

The microstructural evolution of corrosion products directly influences the corrosion rate and failure mode of the material. Three-dimensional reconstruction via focused ion beam-scanning electron microscopy reveals that the corrosion layer on carbon steel in a chloride-containing environment exhibits a typical multilayer structure: an inner layer of amorphous FeOOH with a thickness of 50-100 nm, a middle layer of porous Fe_3O_4 (1-2μm thick), and an outer layer composed of a mixture of acicular α-FeOOH and γ-FeOOH. This structural characteristic results in the corrosion layer possessing significant ion selectivity, with the chloride ion diffusion coefficient in the inner layer being two orders of magnitude higher than in the outer layer[6].

A stochastic model established based on electrochemical noise data indicates that the pitting growth rate and the porosity of the corrosion layer satisfy an exponential relationship. When the porosity increases from 15% to 30%, the pitting propagation rate increases by a factor of 3.8. Quantitative X-ray diffraction analysis shows that when the α-FeOOH/γ-FeOOH ratio increases from 0.5 to 2.0, the corrosion current density decreases by approximately 60%.

Synchrotron radiation X-ray microtomography technology records the real-time three-dimensional morphological evolution of pitting pits. The depth growth of pits follows the relationship $d = kt^n$ (where $n = 0.65 \pm 0.05$), while the diameter expansion conforms to a linear law. Atomic force microscopy demonstrates that the gradient in elastic modulus at the interface between the corrosion layer and the substrate leads to stress concentration. When the layer thickness exceeds 5μm, the interfacial stress reaches 150-200 MPa, promoting cracking and spallation of the corrosion layer.

Conclusion

This study systematically elucidates the transformation behavior of organic chlorides in crude oil and the mechanism by which they induce equipment corrosion through a multi-scale analytical approach. The molecular structure characteristics of organic chlorides determine their transformation pathway selection, with differences in C-Cl bond dissociation energy and spatial configuration leading to specific transformation patterns for different chlorides under thermal and catalytic conditions. The release of hydrogen chloride and its adsorption behavior at the metal interface trigger localized electrochemical corrosion processes, while the selective enrichment of chloride ions at defects in the passive film leads to pitting nucleation and propagation. Analysis of the microstructural evolution of the corrosion layer indicates a quantitative correlation between its multi-layered structural characteristics and the corrosion rate, with interfacial stress concentration promoting cracking and spallation of the corrosion layer. Future research should focus on real-time monitoring technologies for the organic chloride transformation process, characterization of the dynamic evolution behavior at corrosion interfaces, and the design of corrosion-resistant materials based on mechanistic understanding. This will provide new research directions for achieving precise corrosion prevention and control in refining equipment.

References

[1] Duan Yongfeng, Bao Zhenyu, and Wang Ning. "Research Progress on the Occurrence State and Transformation Patterns of Chlorides in Petroleum." Corrosion & Protection in Petrochemical Industry 42.01 (2025): 1-8.

[2] Huang Bingtian. Study on the Adsorptive Removal of Organic Chlorides from Naphtha. 2024. Qingdao University of Science and Technology, MA thesis.

[3] Du Yang. Identification and Removal of Organic Chlorides in Light Distillates of Crude Oil. 2024. China University of Petroleum (Beijing), MA thesis.

[4] Hu Bo, et al. "Research Progress on the Distribution, Transformation, and Hazard of Organic Chlorides in Crude Oil." World Petroleum Industry 31.03 (2024): 90-99.

[5] Guo Jinbiao. "Research Status of Corrosion and Protection by Organic Chlorides in Crude Oil Processing." Materials Protection 54.11 (2021): 173-177.

[6] Wang Guojiang. Study on the Distribution and Transformation of Organic Chlorine from Oilfield Additives during Crude Oil Processing. 2021. China University of Petroleum (Beijing), MA thesis.