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Original Paper

Progress in the Remediation of Heterogeneously Co-Contaminated Petrochemical Soils: From Structural Constraint to Multiscale Process Coupling

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Abstract

Heterogeneously co-contaminated soils impacted by petrochemical activities are characterized by the coexistence of total petroleum hydrocarbons (TPHs), semi-volatile organic compounds (SVOCs), and their weathered derivatives distributed across multiphase soil domains. Their long-term persistence is primarily governed by pore-scale heterogeneity, strong sorption within soil organic matter (SOM), and severe mass transfer limitations across solid–liquid–gas interfaces.This review synthesizes recent advances in understanding and remediating such complex systems from a multiscale and system-coupling perspective. We focus on three interconnected aspects: (i) the structural evolution of contaminated soil matrices under long-term aging, (ii) interfacial activation mechanisms induced by external physical and chemical energy fields, and (iii) the nonlinear coupling among physical transport, chemical transformation, and biological degradation processes.A conceptual framework is proposed, emphasizing "structural constraint release–interfacial activation–system-level evolution", providing theoretical support for hierarchical, adaptive, and energy-efficient remediation strategies in highly heterogeneous contaminated sites.

Keywords

Heterogeneous soil, Petrochemical co-contamination, Interfacial activation, Physicochemical coupling, Hierarchical remediation

1. Introduction

Large-scale petrochemical development over past decades has resulted in widespread soil contamination at industrial sites, including refineries, storage terminals, and chemical manufacturing

areas[1-3]. These sites typically exhibit complex mixtures of total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), and other semi-volatile organic compounds (SVOCs), often coexisting with heavy metals and naturally occurring organic matter[4-6].

Unlike simplified laboratory systems, field-contaminated soils are inherently heterogeneous porous media[7]. Contaminants are distributed across multiple physicochemical states, including:

- Free-phase non-aqueous liquids (NAPLs)[8]
- Dissolved aqueous fractions[9]
- Sorbed phases on mineral surfaces[10]
- Strongly sequestered fractions within condensed soil organic matter[11]

This multi-domain partitioning leads to pronounced non-equilibrium behavior, where contaminant fate is controlled not only by degradation kinetics but also by accessibility constraints imposed by soil structure[12-13].

Conventional remediation technologies such as soil vapor extraction[14,15], in situ chemical oxidation (ISCO)[16,17], thermal desorption[18,19], and bioremediation[20] often assume quasi-homogeneous reaction conditions. However, field performance frequently deviates due to:Preferential flow in high-permeability zones[21]; Diffusion-limited transport in low-permeability domains[22]; Rapid oxidant depletion by non-target soil constituents[23]; Strong aging-induced sequestration within SOM microstructures[24].

These limitations highlight the need to reframe remediation as a multiscale coupled system problem rather than a single-process degradation problem.

Recent research has therefore shifted toward hybrid strategies integrating external energy fields (thermal, microwave, ultrasonic) with chemical oxidation and biological degradation. Despite progress[25-27], a unified theoretical description linking structural evolution, energy transfer, and reaction coupling remains insufficiently developed.

2. Structural Evolution and Mass Transfer Constraints in Contaminated Soils

2.1 Multiphase Heterogeneity and Contaminant Partitioning

Petrochemical-contaminated soils consist of solid mineral frameworks, pore fluids, and gaseous phases forming a triphasic porous system[28]. The spatial distribution of TPHs and SVOCs is strongly influenced by their physicochemical properties, particularly hydrophobicity, molecular weight, and aromaticity[29,30].

Mineral surfaces provide adsorption sites through electrostatic interactions, hydrogen bonding, and van der Waals forces[31]. However, the dominant long-term sink is soil organic matter (SOM), which consists of:

- Labile amorphous carbon fractions (“soft carbon”)[32]
- Condensed aromatic carbon structures (“hard carbon” or black carbon-like domains)[33]

Hydrophobic compounds preferentially partition into SOM due to strong thermodynamic affinity,

particularly via π–π stacking interactions for aromatic hydrocarbons[34]. Over time, this leads to deep sequestration of contaminants into nanoscale organic domains.

2.2 Aging-Induced Structural Immobilization

Long-term weathering fundamentally alters contaminant distribution and soil structure. Labile compounds (e.g., BTEX, short-chain alkanes) are preferentially removed through volatilization, biodegradation, and leaching[35]. The residual fraction becomes increasingly enriched in[36]:

- High molecular weight alkanes
- Resins and asphaltenes
- Condensed multi-ring PAHs

These compounds undergo physicochemical aging processes, including[37]:

- Viscosity increase and phase stiffening
- Formation of hydrophobic coatings on mineral surfaces
- Entrapment within micro- and nano-pores
- Enhanced diffusion resistance in SOM matrices

As a result, the system evolves toward a low-energy, high-barrier state in which contaminant desorption requires significant external energy input.

This aging process is responsible for the well-known "long tail effect" in remediation kinetics, where contaminant concentration declines rapidly initially but stabilizes at a persistent residual plateau.

2.3 Mass Transfer Limitation in Porous Media

Contaminant removal in soil is fundamentally controlled by mass transfer across phase boundaries. A simplified representation of the interphase mass transfer flux (J) can be expressed as follows [38]:

$$J=K_L(C_s^*-C_L)$$

The term Jrepresents the volatile and semi-volatile organic contaminant mass transfer flux across the phase boundary, expressed in $mg\cdot m^{-2}\cdot s^{-1}$, which quantifies the net migration rate of contaminants between solid, liquid, and gas phases.

$K_L$denotes the overall mass transfer coefficient with units of $m\cdot s^{-1}$, which integrates multiple transport resistances within heterogeneous porous media, including the external boundary layer resistance, intra-particle diffusion resistance, and the effects of pore network tortuosity.

C_s^*refers to the equilibrium concentration of the target contaminant in the aqueous phase immediately adjacent to the solid–liquid interface, typically expressed in $mg\cdot L^{-1}$ or equivalently $mg\cdot m^{-3}$. This parameter is governed by the local sorption–desorption equilibrium and reflects the thermodynamically constrained partitioning behavior at the interface.

C_L represents the actual bulk aqueous-phase concentration of the contaminant, also expressed in $mg\cdot L^{-1}$ or $mg\cdot m^{-3}$, and is determined by advective transport, dispersion processes, and ongoing reaction consumption within the aqueous phase.

In aged soils, $K_L$decreases significantly due to:

- Reduced pore connectivity

- Organic film barriers
- Strong intra-particle diffusion resistance

Intra-particle diffusion becomes the rate-limiting step, often several orders of magnitude slower than aqueous-phase transport. Consequently, oxidants or nutrients cannot effectively reach deeply sequestered contaminants.

This mismatch between transport and reaction zones leads to severe inefficiencies in conventional ISCO systems, where reagents are consumed in accessible zones while contaminants in protected domains remain untreated.

3. Interfacial Activation Mechanisms under External Energy Fields

3.1 Energy-Driven Desorption and Structural Disruption

External energy inputs such as heat, microwave radiation, and ultrasonic cavitation are increasingly used to overcome structural constraints in contaminated soils[39].

Thermal activation increases molecular kinetic energy, reducing adsorption stability according to thermodynamic principles. Adsorption coefficients decrease with increasing temperature[40], promoting contaminant release from solid phases.

Microwave irradiation introduces selective heating effects due to dielectric loss differences between soil components[41]. Polar substances and water molecules absorb microwave energy more efficiently, leading to localized overheating and pressure buildup.

This results in:

- Micro-fracturing of soil aggregates[42]
- Disruption of organic coatings[43]
- Enhanced exposure of previously inaccessible contaminant domains[44]

These effects collectively improve reagent accessibility and reaction efficiency.

3.2 Radical-Based Oxidation Chemistry

Advanced oxidation processes (AOPs), particularly persulfate activation systems, generate highly reactive sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals (•OH)[45].

These radicals exhibit strong oxidizing potential and can initiate multiple reaction pathways[46]:

- Electron transfer reactions (SET)
- Radical addition to aromatic rings
- Hydrogen abstraction from aliphatic chains

PAHs are particularly susceptible to electrophilic attack due to their delocalized π-electron systems, leading to ring-opening reactions and formation of oxygenated intermediates[47].

In contrast, aliphatic hydrocarbons exhibit higher bond dissociation energies and lack electron-rich sites, resulting in slower reaction kinetics and reliance on hydrogen abstraction pathways[48].

This intrinsic kinetic disparity contributes to heterogeneous degradation behavior in mixed contaminant systems.

4. Multiscale Coupling of Physical, Chemical, and Biological Processes

4.1 Cross-Scale Functional Hierarchy

Remediation systems operate across interconnected spatial and temporal scales[49]:

- Physical processes: control transport and accessibility (μm–m scale, seconds–hours)
- Chemical processes: govern transformation reactions (nm–μm scale, milliseconds–minutes)
- Biological processes: ensure long-term mineralization (nm–mm scale, days–months)

Each process plays a distinct yet interdependent role in contaminant fate evolution.

Physical processes determine exposure, chemical reactions drive rapid degradation, and biological systems stabilize the final ecological state[50].

4.2 Synergistic and Competitive Mechanisms

When properly coupled, these processes exhibit strong synergy[51]:

- Physical disruption enhances contact efficiency
- Chemical oxidation converts hydrophobic compounds into biodegradable intermediates
- Biological activity completes mineralization under mild conditions

However, improper coupling can induce antagonistic effects[25]:

- Excess oxidation can damage microbial communities
- Over-intensified physical mixing can destabilize soil structure
- Radical overproduction can trigger self-quenching reactions

Such effects highlight the importance of balancing energy input and reaction intensity across scales.

5. Gradient-Based Hierarchical Remediation Strategies

5.1 Spatial Heterogeneity in Field Sites

Contaminated sites typically exhibit strong spatial gradients in both concentration and contaminant form. Core zones are dominated by NAPL accumulation and high toxicity, while peripheral zones contain aged, low-concentration, strongly sorbed residues[52].

This heterogeneity requires differentiated remediation strategies rather than uniform treatment.

5.2 Hierarchical Engineering Framework

A generalized remediation strategy can be structured as:

- Core zones: high-energy treatment (thermal desorption, high-dose ISCO) for rapid mass reduction
- Transition zones: coupled physical–chemical systems (microwave-assisted oxidation, low-dose persulfate)
- Peripheral zones: biological polishing (biostimulation, nutrient amendment, natural attenuation enhancement)

This hierarchical design improves overall efficiency while minimizing ecological disruption and cost.

5.3 Temporal Transition and System Adaptation

Remediation systems should not remain static. As contaminant concentrations decline, the system must transition from aggressive oxidation to biological stabilization.

Failure to adjust process intensity can lead to:

- Microbial inhibition[53]
- Excessive consumption of soil organic carbon[54]
- Reduced long-term sustainability

Therefore, adaptive control based on system state monitoring is essential for optimal performance.

6. Conclusions and Future Perspectives

6.1 Key Findings

Remediation of heterogeneously co-contaminated soils should be understood as a dynamic, multiscale system governed by structural constraints and cross-domain coupling. The main bottleneck lies not in individual degradation reactions but in mass transfer limitations and phase accessibility barriers.

6.2 Future Research Directions

Future work should focus on:

（1） Quantifying contaminant aging mechanisms at molecular and pore scales；

（2） Optimizing external energy fields for selective interfacial activation；

（3） Developing cross-scale coupling models integrating transport, reaction, and biodegradation；

（4） Building intelligent remediation systems capable of adaptive, state-dependent regulation；

Such advances will enable a transition from empirical remediation toward predictive, system-oriented environmental engineering.

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