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Research Progress on Chemical Oxidation Remediation Technologies for Urban Industrial Contaminated Sites — A Perspective on VOCs Pollution Control at the Former Hangzhou Pesticide Factory

Yuening Huang
Hangzhou Xizi Experimental School, Hangzhou, China
Email: yueninghuang1201@163.com

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Abstract

With the acceleration of urbanization in China, contaminated sites left behind by the relocation of numerous industrial enterprises in urban core areas have become major environmental hazards constraining sustainable urban development. Volatile organic compounds (VOCs), owing to their high toxicity, strong volatility, and odor that disturbs residents, represent both a key focus and a significant challenge in the remediation of industrially contaminated sites. This paper takes the VOC contamination and its remediation project at the former pesticide plant in Hangzhou as its starting point, systematically reviews the principles of chemical oxidation remediation technologies, the research progress and current engineering applications of major oxidation systems (Fenton reagent, persulfate, potassium permanganate, ozone, and their combined technologies), analyzes the applicable conditions, advantages, and limitations of each technological system, explores the key factors influencing remediation outcomes, and offers prospects for future development directions. This study aims to provide technical references for decision-making in the remediation of urban industrial contaminated sites, as well as to offer scholarly support for secondary school students to engage in extended learning in the field of environmental science and engineering.

Keywords

Chemical Oxidation Remediation; Soil Contamination; Volatile Organic Compounds; Fenton Reagent; Persulfate; In-Situ Remediation; Hangzhou Pesticide Factory

1. Introduction

1.1. Urban Industrial Contaminated Sites: The Challenge of "Brown

Fields" in the Context of Urbanization

Over the past four decades, China has undergone the largest and fastest urbanization process in human history. The urbanization rate has surged from 17.9% in 1978 to over 67.0% in 2025, and the area of urban built-up zones has expanded nearly tenfold. Within this grand process, policies, such as the withdrawal of the secondary industry from urban core areas, the influx of the tertiary industry into urban core areas, and the relocation of industrial enterprises to industrial parks which have driven tens of thousands of industrial enterprises to move out of urban central areas [1]. However, while factories can be relocated, the pollution remains in place. These abandoned or idle industrial land parcels that whether developed or undeveloped, and whether they pose actual or potential pollution risks are internationally referred to as "Brownfield Sites."

According to the "National Soil Pollution Status Survey Bulletin" jointly issued by the Ministry of Ecology and Environment of China and the former Ministry of Land and Resources in 2014, the overall exceedance rate of soil pollution parameters nationwide was 16.1%, with the exceedance rate in industrial abandoned sites reaching as high as 34.9% [2]. In terms of pollutant types, organic pollutants (including volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), persistent organic pollutants (POPs), etc.) and heavy metals were among the major pollutants. In industrially dense regions such as the Yangtze River Delta, the Pearl River Delta, and the Beijing-Tianjin-Hebei region, the number of sites contaminated by organic pollutants is particularly concentrated.

The hazards posed by contaminated organic sites are multifaceted. First is the health risk: benzene derivatives such as benzene, toluene, and xylene (BTEX) exhibit well-documented carcinogenic and neurotoxic properties, while halogenated hydrocarbons which including trichloromethane and carbon tetrachloride which can cause hepatic and renal dysfunction; organochlorine pesticides, such as hexachlorocyclohexane (HCH) and DDT, are classified as persistent organic pollutants (POPs) with half-lives spanning several decades in the environment, posing threats to ecosystems and human health through bioaccumulation in the food chain [3]. Second is the sensory impact: the volatility of VOCs enables their continuous emission from soil into the atmosphere, generating "chemical off-odors" that can become intolerable for nearby residents, thereby significantly compromising quality of life and potentially triggering social conflicts. Third is the constraint on land value: contaminated sites cannot be repurposed without remediation, leading to prolonged idling of valuable urban land resources and hindering urban renewal efforts.

1.2. Former Hangzhou Pesticide Factory: A Typical Case Study of a VOC-Contaminated Site

Among numerous urban industrial contaminated sites, the former pesticide plant in

Hangzhou (Sanliting site) has become an excellent window for observing the remediation of organic contaminated sites in China, owing to its distinctive contamination characteristics and the high-profile nature of its remediation process. The Hangzhou Pesticide Factory was established in 1958 and is located in the Sanlitong area of eastern Hangzhou (at the intersection of Shiqiao Road and Xinfeng Road), covering a site area of approximately 147,000 square meters. The factory is a key enterprise in China's pesticide industry, primarily producing organochlorinated pesticides (hexachloroethane raw powder and its various isomers, DDT raw powder) and organophosphorus pesticides (dichlorvos, dimethoate, oxidized dimethoate, etc.); at its peak, its annual output ranked fourth nationwide [4]. In 2009, in accordance with the urban planning of Hangzhou, the pesticide factory officially ceased operations and relocated.

The environmental investigation of the site following its relocation revealed that the contamination depth in this plot extends to 8–12 meters below ground level, and various VOCs and SVOCs were detected in the soil. The primary categories of pollutants include: (1) BTEX compounds—toluene, xylene, ethylbenzene, etc. That originating from the use of organic solvents in pesticide production processes; (2) halogenated hydrocarbons—dichloromethane, chloroform, carbon tetrachloride, etc. which are commonly used reagents and by-products in pesticide synthesis processes; (3) organochlorinated pesticides—α-HCH, β-HCH, γ-HCH, δ-HCH, p, p'-DDT, p, p'-DDE, p, p'-DDD, etc. which are direct residues of the core products [5]. Most of these substances fall under the category of VOCs; they exhibit relatively high vapor pressures at room temperature and are the primary contributors to the odorous characteristics of the site.

In 2014, the remediation project on this site was launched, immediately drawing widespread public attention. To prevent large-scale releases of VOCs caused by excavation work, the construction contractor erected a white inflatable membrane structure - 36 meters high with a coverage area of approximately 20,000 square meters in the most heavily contaminated area; this structure maintained negative pressure internally and was equipped with an activated carbon exhaust gas treatment system [6]. This facility, costing approximately 16 million yuan, was dubbed by the media as "the largest toxic gas tent in history," becoming a focal point of national public discourse at the time and bringing soil remediation, a relatively niche field within environmental protection into the public eye.

The remediation of the Hangzhou Pesticide Plant employed a combined process route consisting of "Ex-situ Thermal Desorption + Chemical Oxidation" [7]. Thermal desorption was used to treat soils with high contaminant concentrations; by heating the soil to 300–500 °C, VOCs were desorbed and volatilized from the soil matrix, after which they were collected and treated. Chemical oxidation, in contrast, was applied to areas with medium-to-low contaminant concentrations and to the "tail" residues remaining after thermal desorption, where strong oxidants were injected

to degrade organic compounds in situ.

This case study highlights the core challenges of remediating urban contaminated sites: how to safely, efficiently, and economically eliminate VOCs from soil within densely populated urban environments,not only addressing long-term health risks but also mitigating secondary pollution during remediation operations (particularly the dispersion of odors).

1.3. Positioning and Research Significance of Chemical Oxidation Remediation Technology

Within the technological spectrum of soil remediation, chemical oxidation remediation occupies a distinctive position. Compared to physical remediation methods, such as excavation and landfilling, thermal desorption, and soil gas extraction that chemical oxidation can be implemented in-situ, eliminating the need for large-scale excavation and transport, while causing minimal disturbance to the soil surface; this makes it particularly suitable for urban built-up areas. Relative to bioremediation approaches, such as microbial degradation and phytoremediation—chemical oxidation exhibits reaction rates several orders of magnitude higher, reducing remediation durations from months or even years to just days or weeks. Furthermore, compared to Monitored Natural Attenuation, chemical oxidation represents an active intervention strategy, offering greater predictability of remediation outcomes [8].

For this reason, chemical oxidation remediation technology has evolved from laboratory research to engineering practice over the past three decades, becoming one of the mainstream technologies for the remediation of contaminated organic sites. According to statistics from the U.S. Environmental Protection Agency (US EPA) Superfund program, among the contaminated site remediation projects completed between 1982 and 2017, cases utilizing In Situ Chemical Oxidation (ISCO) technology accounted for approximately 12% of groundwater remediation projects and approximately 8% of soil remediation projects, with a consistent year-on-year upward trend [9].

However, chemical oxidation is not a "panacea." Different oxidation systems exhibit significant differences in reaction mechanisms, degradation profiles, applicable conditions, and engineering performance; factors such as soil heterogeneity, organic matter content, pH buffering capacity, and water content exert complex influences on the transport and reaction of oxidants; and the "contact" issue between oxidants and pollutants;namely, that pollutants may be "trapped" within soil micropores and organic matter, making them difficult for oxidants to reach, that is a classic challenge in in-situ remediation [10].

Therefore, systematically reviewing the principles, advancements, application cases, and future trends of chemical oxidation remediation technologies is of great significance for promoting the scientific application of such technologies. Using the

VOCs pollution at the Hangzhou Pesticide Plant as a case study, this paper reviews the research and application progress of three mainstream chemical oxidation systems (Fenton reagent, persulfate, potassium permanganate) and ozone-based technologies, compares their respective advantages and disadvantages, summarizes the key influencing factors, and outlines future development directions.

2. Overview of the Principles of Chemical Oxidation Remediation Technology

2.1. Basic Concepts of Chemical Oxidation

The fundamental principle of chemical oxidation remediation is to inject chemical oxidants into contaminated soil or groundwater, leveraging the redox reaction between the oxidants and organic pollutants to oxidatively degrade organic molecules, under ideal conditions achieving "complete mineralization," whereby the organic matter is fully converted into carbon dioxide (CO_2), water (H_2O), and inorganic ions.

Taking the complete mineralization of benzene (C_6H_6, a representative VOC) as an example, the overall reaction can be expressed as follows:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

However, although this overall reaction is thermodynamically spontaneous ($\Delta G < 0$), it proceeds extremely slowly kinetically, because benzene hardly reacts with molecular oxygen under ambient temperature and pressure. The essence of chemical oxidation remediation is to introduce a strong oxidant whose reactivity far exceeds that of molecular oxygen, thereby kinetically "opening" reaction pathways and enabling the degradation process to complete within an engineering-acceptable time frame [11].

2.2. Free Radical Oxidation and Non-Free Radical Oxidation

Depending on the reaction mechanism, chemical oxidation can be classified into two major categories: free-radical oxidation and non-free-radical (direct) oxidation.

Free radical oxidation refers to the process in which an oxidizing agent attacks organic molecules by generating highly reactive free radicals, primarily hydroxyl radicals (·OH) and sulfate radicals ($\cdot SO_4^-$). Free radicals possess one or more unpaired electrons and exhibit a strong propensity to acquire electrons to form electron pairs; consequently, they exhibit exceptionally high reactivity. The standard oxidation-reduction potential (E°) of ·OH is +2.80 V, second only to that of fluorine gas (+3.06 V), enabling it to react with the vast majority of organic compounds at rates approaching the diffusion-controlled limit ($k \approx 10^8$–10^{10} $M^{-1}\cdot s^{-1}$) [12]. Characteristic features of free radical reactions include low selectivity (essentially "non-selective attack"), rapid reaction rates, and chain propagation. The Fenton

reagent and activated persulfate are representative examples of free radical oxidation systems.

Non-radical oxidation involves the direct electron transfer between the oxidizing agent molecule and the organic compound, without the involvement of radical intermediates. Potassium permanganate (MnO_4^-) is a classic example of this mechanism: MnO_4^- is reduced to Mn^{2+} (under acidic conditions) or to MnO_2 (under neutral/alkaline conditions) by accepting five electrons, while the organic compound is oxidized in this process. Non-radical oxidation is characterized by high reaction selectivity (preferential attack on organic compounds bearing specific functional groups, such as carbon-carbon double bonds, C=C), relatively slow reaction rates, and high oxidizing agent utilization efficiency [13].

Understanding these mechanistic differences is crucial for elucidating the performance characteristics of different oxidation systems, serving as the foundation for the comparative analysis presented later.

2.3. Technical Selection Between In Situ Repair and Ex Situ Repair

Chemical oxidation remediation can be carried out via two approaches: in-situ or ex-situ.

In-situ Chemical Oxidation (ISCO) involves injecting an oxidant solution directly into an underground contaminated zone via a downhole injection well or a push-type drilling rig; the oxidant then migrates and diffuses through the soil pores, where it reacts with the contaminants. The advantages of ISCO include the absence of large-scale excavation, minimal surface disturbance, the capability to be implemented beneath structures, and relatively controllable environmental impacts on surrounding areas during construction. However, its challenges stem from the heterogeneity of the subsurface environment, which can lead to unpredictable oxidant transport pathways and the potential occurrence of "fingering" where the oxidant migrates along preferential flow paths, leaving contaminants in low-permeability zones unexposed to the oxidant [14].

Ectopic chemical oxidation involves excavating contaminated soil to the surface and then mixing it with an oxidizing agent in specialized reaction vessels or dedicated storage facilities. Its advantage lies in the controllable reaction conditions (e.g.stirring to ensure thorough mixing, and adjustable parameters such as pH and temperature); however, its drawbacks are also significant: substantial releases of VOCs during excavation (as exemplified by the "toxic gas tents" at the Hangzhou pesticide plant, which were specifically designed to address this issue), high costs associated with soil transportation, and the impracticality of excavating deeply contaminated soil.

The combined approach of "ex-situ thermal desorption + chemical oxidation" adopted by the Hangzhou Pesticide Factory belongs to the ex-situ remediation pathway, with the chemical oxidation stage primarily targeting residual

low-concentration contaminants following thermal desorption. Regarding the feasibility of in-situ implementation, the rationale for selecting the ex-situ approach over ISCO for this site includes the following factors: (a) the extent of contamination is relatively deep (8–12 m), making it difficult to ensure uniformity of in-situ injection; (b) the site is zoned for mixed residential and commercial use, requiring high soil quality standards (Class I land use criteria), necessitating the controllable nature of ex-situ treatment; (c) the underground utility network in the urban built-up area is highly complex, limiting the feasibility of in-situ injection [15].

3. Research Progress on Major Chemical Oxidation Systems

3.1. Fenton Reagent and Its Derivative Systems

(1) Classical Fenton reagent

In 1894, the French chemist Henry J. Fenton discovered that in acidic conditions, a mixture of H_2O_2 and Fe^{2+} exhibits exceptionally strong oxidizing capacity and can degrade a variety of organic compounds—a reaction that was later named the "Fenton reaction." More than a century later, the Fenton reagent has become one of the most widely used chemical oxidation systems in the field of environmental remediation.

The core of the Fenton reaction is the Fe^{2+}-catalyzed decomposition of H_2O_2 to generate ·OH:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (k \approx 76\ M^{-1}s^{-1})$$

The generated ·OH rapidly reacts with organic compounds (RH):

$$\cdot OH + RH \rightarrow \text{oxidative product}$$

Simultaneously, a redox reaction ($Fe^{3+} \rightarrow Fe^{2+}$) occurs (ensuring the maintenance of the catalytic cycle):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot + H^+ \quad (k \approx 0.01\ M^{-1}s^{-1})$$

The key advantages of Fenton's reagent are: · the strong oxidizing capacity of ·OH, a rapid reaction rate, and the low cost of the reagents（H_2O_2 and $FeSO_4$）. Its primary limitation, however, is that the optimal pH range for the reaction is extremely narrow (pH 2.8–3.5); if this range is deviated from, Fe^{3+} will precipitate, or the yield of ·OH will drop sharply [16].

In soil remediation applications, a specific challenge faced by Fenton reagents is that natural soils typically exhibit substantial pH buffering capacity (provided by the protonation/deprotonation reactions of carbonates and layered silicates), which requires the consumption of large amounts of acid to maintain a pH of approximately 3; concurrently, soil organic matter (SOM) acts as a potent scavenger of ·OH, leading to the non-productive consumption of substantial quantities of oxidants by SOM [17]. Studies have demonstrated that when Fenton reagents are

applied in soils with organic matter content exceeding 5%, as much as 70–90% of the ·OH is scavenged by SOM rather than by target pollutants [18].

(2) Modified Fenton and Fenton-like systems

To overcome the pH limitations of the classical Fenton process and the interference caused by SOM, researchers have developed a series of modified systems:

Chelated iron Fenton: By employing chelating agents such as citric acid, ethylenediaminetetraacetic acid (EDTA), or nitrotriacetic acid (NTA) to form soluble complexes with Fe^{2+}/Fe^{3+}, the solubility and catalytic activity of iron ions are maintained under neutral pH conditions [19]. Chelated iron Fenton extends its applicable pH range to 5–9, significantly enhancing its practical applicability in soil remediation; however, the chelating agents themselves are also oxidized and consumed, thereby increasing reagent costs.

Mineral-catalyzed Fenton reaction: The surfaces of naturally occurring iron oxide minerals in soil (e.g., goethite α-FeOOH, magnetite Fe_3O_4) are utilized as heterogeneous Fenton catalysts. This scheme boasts three distinct advantages: no requirement for additional dissolved iron salts, zero secondary pollution as the catalysts are natural minerals, and adaptability to neutral pH conditions. Nevertheless, its catalytic efficiency is generally lower than that of homogeneous Fenton reactions, with a relatively slow reaction rate [20].

Electro-Fenton: This process generates H_2O_2 in situ via electrochemical reactions at an electrode (cathodic oxygen reduction: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) while simultaneously reducing Fe^{3+} to Fe^{2+}, thereby enabling "on-demand generation" of oxidants and catalyst recycling. Electro-Fenton mitigates the storage and transportation safety risks associated with high-concentration H_2O_2; however, due to the requirement for electrode infrastructure, it is primarily employed in groundwater treatment (after extraction to the surface for processing), whereas its application in in-situ soil remediation remains limited [21].

3.2. Persulfate Activation System

(1) Chemical Properties of Persulfate

Persulfates include persulfonic acid (PMS, HSO_5^-) and persulfate (PS, $S_2O_8^{2-}$), with sodium persulfate ($Na_2S_2O_8$) being the most commonly used in environmental remediation. The persulfate anion $S_2O_8^{2-}$ itself possesses certain oxidizing properties ($E° = +2.01$ V), but its direct reaction rate with most organic compounds is relatively slow. Upon appropriate activation, the O–O bond in the $S_2O_8^{2-}$ molecule cleaves, generating a sulfate radical ($SO_4^{-}\cdot$):

$$S_2O_8^{2-} \xrightarrow{\text{activate}} 2SO_4^{-\cdot}$$

$SO_4^{-}\cdot$ exhibits the following remarkable properties: (a) strong oxidizing capability, with $E°$ ranging from +2.60 to +3.10 V (depending on pH and measurement methodology), comparable to or even exceeding that of ·OH (+2.80 V); (b) a half-life

of approximately 30–40 μs, significantly longer than that of ·OH (<1 μs), enabling it to travel greater distances within soil matrices; (c) a reaction mechanism dominated by electron transfer (whereas ·OH primarily relies on hydrogen abstraction and electrophilic addition), conferring high reaction selectivity toward organic compounds containing aromatic rings and unsaturated bonds [22].

(2) Research Progress on Activation Methods

Persulfate requires activation to efficiently generate $SO_4^{-}\cdot$, and the activation method is a critical variable influencing its remediation performance. Currently, the most extensively studied activation methods include:

Transition metal activation, and Fe^{2+} is the most commonly used:

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + Fe^{3+}$$

Fe^{2+} activation offers high efficiency and low cost; however, it is subject to pH limitations similar to those of Fenton reagents (acidic conditions inhibit Fe^{2+} precipitation) and side reactions involving excessive consumption of $SO_4^{-}\cdot$ by Fe^{2+} ($SO_4^{-}\cdot + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+}$, $k \approx 4.6\times10^9$ $M^{-1}\cdot s^{-1}$). In recent years, research focus has shifted toward slow-release iron sources, such as nanoscale zero-valent iron (nZVI) and iron-based bimetallic nanoparticles, to enable gradual and sustained release of Fe^{2+}, thereby reducing the self-consumption of active free radicals [23].

Thermal activation — heating to 40–99 °C to induce thermal cleavage of the O–O bond:

$$S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^{-\cdot}$$

Thermal activation requires no external chemical activators, thereby avoiding secondary contamination and chemical reagent costs. However, its application in soil remediation is limited by heating energy consumption and the control of subsurface temperature field homogeneity. In-Situ Thermal Activation (iSTAP), which combines resistive heating or steam injection with persulfate injection, represents a cutting-edge approach in this field [24].

Alkaline activation—under high pH (>11) conditions:

$$S_2O_8^{2-} + \rightarrow SO_4^{-\cdot} + SO_4^{2-} + H_2O$$

Alkaline activation also generates secondary reactive species, such as superoxide radicals ($O_2^{-}\cdot$), and demonstrates superior degradation efficacy for certain pollutants compared to systems relying solely on SO_4^{-}. However, high pH conditions themselves may trigger the activation and release of heavy metals and alter the mineral structure of soil; therefore, careful evaluation is warranted [25].

Furthermore, various activation methods—including UV light activation, ultrasonic activation, microwave activation, and biochar-catalyzed activation—have been investigated and reported at the laboratory scale; however, most of these approaches have not yet entered the stage of engineering application [26].

3.3. Potassium permanganate system

Potassium permanganate ($KMnO_4$) is one of the chemically oxidizing agents with the longest history of use in soil remediation. Unlike the Fenton process and persulfate-based methods, $KMnO_4$ does not rely on free radical intermediates; instead, it oxidizes organic compounds via direct electron transfer. Under acidic conditions, the half-reaction is as follows:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad (E^\circ = +1.51\,V)$$

Under neutral or alkaline conditions, the reduction product is a precipitate of MnO_2:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 \downarrow + 4OH^- \quad (E^\circ = +0.59\,V)$$

The following properties of $KMnO_4$ confer unique value to its application in soil remediation:

High selectivity: MnO_4^- exhibits an extremely fast reaction rate ($k \approx 10^0$–$10^1\ M^{-1}\cdot s^{-1}$) toward unsaturated compounds containing C=C bonds (e.g., chlorinated hydrocarbons such as trichloroethylene (TCE) and perchloroethylene (PCE), whereas its reaction rate toward saturated alkanes and benzene rings is exceedingly slow ($k < 10^{-5}\ M^{-1}\cdot s^{-1}$). This high selectivity presents both advantages—enabling "precision targeting" of target pollutants and high oxidant utilization efficiency and limitations which resulting in poor degradation performance for pollutants such as BTEX that lack reactive double bonds [27].

Long-lasting efficacy: $KMnO_4$ exhibits a relatively slow natural degradation rate in soil and groundwater environments (primarily due to unintended consumption by reducible minerals), allowing it to persist for several weeks to months. This means that a single injection can maintain oxidative capacity over an extended period, making it particularly suitable for addressing the "rebound" phenomenon that namely, the slow release of adsorbed or non-aqueous phase liquid (NAPL)-phase pollutants following cessation of remediation efforts, which can lead to a resurgence in contaminant concentrations [28].

Visibility: The $KMnO_4$ solution exhibits a deep purple color, allowing its subsurface migration path to be tracked via coloration, thereby facilitating in-situ monitoring, a distinct advantage not possessed by other colorless oxidants.

The primary challenges encountered when using $KMnO_4$ in engineering applications are as follows: (a) the MnO_2 precipitate formed during the reaction may clog soil pores, reducing permeability and limiting the subsequent injection of oxidants [29]; (b) in acidic soils, the generation of Mn^{2+} may lead to groundwater manganese concentrations exceeding permissible limits (drinking water manganese standard: 0.1 mg/L); (c) the oxidizing capacity of MnO_4^- significantly decreases under alkaline conditions.

3.4. Ozone and Other Oxidation Systems

Ozone (O_3): Ozone is a gaseous oxidant (E° = +2.07 V) that can be delivered to unsaturated soil layers (the vadose zone) via gaseous injection. The advantages of ozone include: gaseous transport overcomes the permeability limitations of liquid oxidants, enabling rapid diffusion in unsaturated soil; ozone can naturally decompose into O_2, leaving no chemical residues. Its limitations are: ozone generation requires on-site gas generation equipment, involves high energy consumption, and offers limited efficacy in remediating pollutants within the saturated zone (groundwater), owing to its low solubility in water and rapid decomposition rate [30].

Combination/Sequential Oxidation: In recent years, the combined application of diverse oxidation systems has become a research hotspot. For example, sequential injection of "persulfate + potassium permanganate"—first treating highly reactive double-bond pollutants such as TCE with $KMnO_4$ (leveraging the high selectivity of $KMnO_4$), followed by treatment of residual low-reactivity pollutants like BTEX with activated persulfate (utilizing the broad-spectrum activity of $SO_4^{-}\cdot$). Another strategy involves the combined use of "Fenton + persulfate" where Fenton generates ·OH for rapid initiation of degradation, while persulfate provides $SO_4\cdot^{-}$ to sustain prolonged oxidative capacity [31].

3.5. Comprehensive Comparative Analysis of the Various Systems

Table 1. Comparison of Performance Characteristics of Major Chemical Oxidation Systems

Comparison Dimensions	Fenton reagent	Activated persulfate	Potassium permanganate	Ozone
Active species	·OH	$SO_4^{-}\cdot$	MnO_4^{-} (direct)	O_3
E°(V)	+2.80	+2.60~3.10	+1.51 (acidic)	+2.07
mechanism of a reaction	Free radical chain reaction	Free radical chain reaction	Direct electron transfer	Direct + free radical
reaction selectivity	Extremely low (broad-spectrum)	Low to medium	Gao	Middle
the best pH	2.8~3.5	2~9	neutral	Neutral to alkaline
Subterranean durability	Several minutes to several hours	Several days to several weeks	Several weeks to several months	Several dozen minutes
Main by-products	$Fe(OH)_3$, organic intermediates	SO_4^{2-}, organic intermediates	$MnO_2\downarrow$, Mn^{2+}	O_2(harmless)
Drug costs	low	Middle	higher	Medium (power consumption)
Technical maturity	High (widely applied)	High (rapid growth)	High (long history)	Middle
Number of literature cases	>500 articles	>300 articles	>400 articles	>200 articles

4. Key Factors Affecting the Efficacy of Chemical Oxidation Remediation

The effectiveness of chemical oxidation remediation is influenced by the combined effects of multiple factors; understanding these factors is crucial for the scientific design and optimization of remediation strategies. This section examines these factors from three perspectives: soil characteristics, pollutant characteristics, and process parameters.

4.1. Influence of Soil Physicochemical Properties

(1) Soil organic matter (SOM)

SOM is one of the most critical factors influencing chemical oxidation efficiency. SOM consists of complex organic macromolecules, such as humic acids, fulvic acids, and humins, and is inherently a reducing agent. When an oxidant is introduced to the soil, SOM competes with target pollutants for the oxidant, a process known as "Natural Oxidant Demand" (NOD) or "Soil Oxidant Demand" (SOD) [32].

Different oxidation systems exhibit varying sensitivities toward SOM. ·OH, owing to its extremely low reaction selectivity, is quenched by SOM in the highest proportion; MnO_4^- demonstrates relatively low reactivity toward the saturated fatty acid carbon chains abundant in SOM, and its SOD activity is comparatively low. Studies have reported that in soils containing SOM at concentrations ranging from 3% to 30%, the SOD activity of the Fenton reagent can reach 10–100 times the theoretical oxidant demand for pollutants, whereas that of potassium permanganate ranges from 2 to 20 times, and that of persulfate falls intermediate between the two [33].

(2) Soil pH and buffering capacity

As previously mentioned, pH exerts the most pronounced effect on the Fenton reagent—when pH exceeds 4, Fe^{3+} precipitates, thereby disrupting the catalytic cycle. The buffering capacity of soil in response to pH changes (primarily determined by carbonate content and cation exchange capacity) dictates the amount of acid required in practical remediation efforts to maintain the acidic conditions necessary for the Fenton reaction. Limestone soils with high carbonate content are highly unfavorable for Fenton processes [16].

Persulfate exhibits activity across a pH range of 2–9, demonstrating the greatest adaptability to soil pH levels. However, extreme alkaline conditions (pH > 11; e.g., alkaline activation of persulfate) may cause irreversible damage to soil ecosystems. Potassium permanganate exhibits stronger oxidizing capacity under acidic conditions but may lead to excessive Mn^{2+} accumulation; under neutral conditions, its oxidizing capacity decreases, while the risk associated with the byproduct MnO_2 is relatively low [27].

(3) Soil texture and permeability

Permeability determines the transport efficiency of the oxidant solution within the soil. In coarse-textured soils (e.g.,), sandy soil), permeability is high, allowing the oxidant to distribute rapidly and uniformly, but resulting in a short residence time; in fine-textured soils (e.g.clay soil), permeability is low, leading to slow transport of

the oxidant or even preventing effective infiltration, although once the oxidant enters the soil, its residence time is prolonged. An ideal site for in-situ chemical oxidation typically exhibits moderate permeability (hydraulic conductivity K ≈ 10^{-3}–10^{-5} cm/s), providing both sufficient transport rate and adequate contact time [14].

Soil heterogeneity, namely the variation in soil properties across different depths and locations which represents one of the greatest challenges in in-situ remediation projects. Sandy lenses may serve as preferential pathways for oxidants, whereas pollutants within clay lenses are scarcely accessible.

4.2. Influence of Pollutant Characteristics

(1) Chemical structure of the pollutants

The reaction rates of oxidizing agents toward organic compounds with different chemical structures can differ by several orders of magnitude. Taking ·OH as an example, its reaction rate constant with benzene is k = 7.8 × 10^9 $M^{-1}·s^{-1}$, whereas its reaction rate constant with chloroform ($CHCl_3$) is k = 5.4 × 10^7 $M^{-1}·s^{-1}$, a difference of approximately 140-fold [34]. The reaction selectivity of SO_4^{-}· lies between that of OH^- (no selectivity) and MnO_4^- (high selectivity): it exhibits high reaction rates toward aromatic compounds bearing electron-donating groups (-OH, -NH_2, -OR), while its reaction rates toward compounds bearing electron-withdrawing groups (-NO_2, -Cl, -COOH) are relatively lower [22].

The practical significance of this difference lies in the fact that, for mixed-polluted sites (which constitute the vast majority of real-world sites), a single oxidation system often cannot achieve equally high degradation efficiency for all target pollutants; therefore, "combined oxidation" is a necessary strategy.

(2) Speciation of pollutants

The speciation of organic compounds in soil that dissolved phase, adsorbed phase, and non-aqueous liquid (NAPL) phase which significantly influences their contact with and reaction with oxidants. Dissolved organic compounds are most readily accessible to oxidants; adsorbed organic compounds are retained by soil organic matter or clay minerals, and their desorption rate may become the rate-limiting step for degradation [35]; NAPL-phase organic compounds (i.e., pollutants existing as discrete oil phases in highly contaminated areas) act as persistent pollution sources, slowly dissolving during remediation to replenish aqueous-phase concentrations, which is the primary cause of the "rebound" phenomenon.

In the VOCs contamination at the Hangzhou Pesticide Plant, certain high-concentration areas may contain residual organic solvents in NAPL form; this is why a staged treatment approach was selected for this site the first employing thermal desorption to remove high-concentration NAPL-based contamination, followed by chemical oxidation treatment to address residual dissolved or adsorbed contamination.

4.3. Influence of Process Parameters

(1) Oxidant dosage

The dosage of the oxidant is the core parameter in the design of a remediation strategy. Insufficient dosing may lead to incomplete degradation, whereas excessive dosing can result in reagent waste and potentially trigger unwanted side reactions. The theoretical oxidant requirement can be calculated based on the stoichiometric ratio of the pollutants; however, in practical applications, it is often necessary to significantly increase the dosage using SOD. In routine engineering practice, the oxidant dosage typically ranges from 2 to 10 times the stoichiometric requirement [32]. In recent years, there has been a growing trend toward adopting a "staged injection" strategy instead of a single high-dose injection, thereby minimizing non-target consumption of the oxidant and enhancing utilization efficiency.

(2) Injection method

Common injection methods for oxidants include direct-push injection, injection wells, and permeable reactive barriers. The injection pressure and flow rate must be precisely designed based on the soil permeability: excessively high pressure may induce "hydraulic fracturing" in the soil, creating uncontrolled preferential flow pathways; conversely, an excessively high flow rate can lead to excessive concentration of the oxidant near the injection well, resulting in an "insufficient radius"—where the effective impact zone is significantly smaller than the designed value [36].

(3) Use of catalysts/activators

For persulfate systems, the selection of activators and their dosing strategy are critical factors in determining remediation efficacy. The "one-step method" using Fe^{2+} activation, where persulfate and Fe^{2+} are injected simultaneously which offers simple operation; however, Fe^{2+} is rapidly oxidized in the vicinity of the injection well, leading to localized generation of $SO_4^{-}\cdot$ within the well perimeter and limiting its transport radius. In contrast, the "two-step method" or "sequential injection" in which a persulfate solution devoid of activators is first injected into the target zone, followed by the injection of the activator, enables $SO_4^{-}\cdot$ to be generated over a broader spatial range [37]. Furthermore, iron chelated with citrate has gained increasing adoption in engineering applications, as it maintains the solubility of Fe^{2+} under neutral pH conditions while slowing the oxidation rate of Fe^{2+}.

5. Engineering Practices and Representative Cases of Chemical Oxidation Remediation

5.1. Overview of International Engineering Practice

The in-situ chemical oxidation (ISCO) technology has been employed in engineering applications across North America for over three decades. According to statistics from the US EPA Superfund Program, ISCO is most widely used in the remediation of sites contaminated by chlorinated solvents (e.g.TCE, PCE), accounting for over 60%

of ISCO cases; it is followed by sites contaminated by fuel hydrocarbons (BTEX and MTBE), accounting for approximately 20% [9].

Regarding the selection of oxidants, the early ISCO projects in the United States primarily utilized potassium permanganate (from the 1990s to the early 2000s) due to its simple operation, excellent visual monitoring capabilities, and long subsurface persistence; since the mid-2000s, the application of activated persulfate has grown rapidly, and it has now surpassed potassium permanganate to become the most commonly used ISCO oxidant—driven by its superior degradation capacity for BTEX and MTBE, broader pH adaptability, and advancements in activation technologies. The use of Fenton reagents in ISCO applications remains relatively limited, primarily constrained by the engineering challenges of pH control; they are instead more frequently employed in ex-situ remediation (e.g., treating groundwater extracted from reactors) [38].

The soil remediation market in Europe exhibits varying technical preferences due to differences in national regulations. In the Netherlands and Denmark, in-situ bioremediation is the primary approach (accounting for over 50% of remediation projects), while chemical oxidation serves as a supplementary method [39]; in Germany and France, there is relatively high acceptance of chemical oxidation, but this is constrained by stringent groundwater manganese standards (the EU drinking water manganese standard is 0.05 mg/L, which is stricter than both the U.S. Category II standard of 0.05 mg/L and China's standard of 0.1 mg/L), thereby limiting the application of $KMnO_4$.

5.2. Practical Progress in the Remediation of Organic-Contaminated Sites in China

China's soil remediation industry started relatively late but has developed rapidly. Taking the 2004 poisoning incident among workers at the Beijing Songjiazhuang subway project and the 2006 pollution incident at the Heshan site in Wuhan (formerly the Wuhan Pesticide Factory) as landmark events, the issue of contaminated sites has come into the focus of both the public and policymakers. In 2016, the State Council of China issued the "Soil Pollution Prevention and Control Action Plan" ("Ten Measures for Soil Pollution Prevention and Control"), and in 2019, the "Soil Pollution Prevention and Control Law" officially came into effect, marking the entry of China's soil remediation sector into a phase of rule-of-law governance and large-scale implementation [40].

In the field of chemical oxidation, research and engineering practices in China exhibit the following characteristics:

(1) Composite pollution has become the norm: pollution at industrial sites in China is often more complex than the "single pollutant, single source" scenarios in Europe and the United States. Taking pesticide chemical plants as an example, these sites frequently harbor multiple pollutants simultaneously, including VOCs, SVOCs, and

heavy metals. This poses greater demands on chemical oxidation processes—oxidizing agents must be capable of addressing more complex pollutant profiles.

(2) Urban high-density environmental constraints: The building density and population density in China's urban built-up areas are generally higher than those in Europe and North America, making the "NIMBY effect" in remediation projects even more pronounced. The "toxic gas tent" incident at the Hangzhou pesticide plant serves as a typical case—public heightened sensitivity to odors during construction has compelled the implementation of stringent odor control measures. This has driven the Chinese remediation industry to place greater emphasis on the development of "low disturbance" remediation technologies, including technical approaches such as ISCO and the combined use of surfactants for enhanced solubility followed by chemical oxidation [41].

(3) Promotion of industry-university-research integration: Research institutions, including Zhejiang University, Tsinghua University, and the Nanjing Institute of Soil Science of the Chinese Academy of Sciences, have conducted extensive research in the field of chemical oxidation remediation and facilitated the commercialization of related technologies. For instance, Professor Yang Kun's research team at Zhejiang University addressed the odor control challenge at a pesticide plant site in Hangzhou by developing "In-situ Barrier and Inhibition Microcrystalline Powder Material for Soil Odors." This material achieves in-situ odor control through the physical blocking and chemical adsorption of VOC molecules by its mineral microcrystalline layers, and has already established a production line with an annual capacity of 5,000 tons [42]. This case exemplifies the "reverse research" approach that starting from practical problems to drive technological solutions.

5.3. Case Study

(1) Hangzhou Former Pesticide Factory (Zhejiang, China)

As previously discussed, this section provides a summary from a technical evaluation perspective. The site covers approximately 147,000 m^2, with the primary pollutants being BTEX, halogenated hydrocarbons, and organochlorinated pesticides. The remediation strategy consists of "ex-situ thermal desorption (for high-concentration zones) + chemical oxidation (for medium-to low-concentration zones) + gas-phase extraction (for VOC emission control)." Following remediation, the site has been rezoned for mixed residential and commercial use. The value of this case study lies in: (a) demonstrating the complete remediation process for large contaminated sites in urban built-up areas; (b) highlighting the engineering challenges and corresponding solutions for VOC odor control; and (c) validating the applicability of the thermal desorption combined with chemical oxidation approach for sites contaminated by pesticides and chemicals [7].

(2) Wuhan Heshan Plot (formerly Wuhan Pesticide Factory) (Hubei, China)

The contaminated area of the Heshan site in Wuhan covers approximately 240,000 m^2, with the primary pollutants being organochlorinated pesticides (hexachlorocyclohexane isomers and DDT analogs) and organophosphorus pesticides, making it one of the largest pesticide-contaminated sites in China. In 2006, construction of affordable housing began on this site without prior remediation, during which construction workers exhibited poisoning symptoms, triggering widespread public concern. Following this incident, the site was urgently cordoned off, and comprehensive remediation efforts were initiated. The project adopted a remediation strategy primarily based on thermal desorption, supplemented by chemical oxidation, with a remediation duration spanning several years and a total investment exceeding several billion yuan, thereby establishing it as a "textbook" case in soil remediation in China. The key lesson from this case is that the consequences of developing and constructing a contaminated site without prior remediation can be extremely severe [43].

(3) Case Study of In Situ $KMnO_4$ Remediation of a TCE-Contaminated Site in the United States

At the former site of a semiconductor manufacturing plant in Florida, United States, extensive groundwater contamination by trichloroethylene (TCE) was identified, with a contaminant plume extending approximately 2 km, posing a threat to downstream drinking water sources. Between 2002 and 2008, this site underwent multiple rounds of in-situ $KMnO_4$ injection remediation, with a cumulative injection volume of approximately 2 million gallons (≈7,500 m^3) of $KMnO_4$ solution at concentrations ranging from 2% to 4%. Monitoring data indicate that the TCE concentration in the contaminated area decreased from 15,000 μg/L prior to injection to below 50 μg/L after remediation, achieving a removal efficiency of 99.7%; however, a low-concentration "tail" persisted at the terminus of the contaminant plume, highlighting the limitations of ISCO for treating low-concentration, large-area contaminations [44].

The key takeaway from this case is that chemical oxidation demonstrates remarkable efficacy in reducing the "mass flux" of high-concentration pollutants within contaminated source areas; however, relying solely on chemical oxidation to achieve complete remediation which ensuring that "every drop meets the standards" is unrealistic. Instead, it is necessary to integrate passive technologies, such as Monitored Natural Attenuation (MNA), to address residual pollutants at low concentrations.

6. Challenges and Development Trends in Chemical Oxidation Remediation

6.1. Key Challenges Currently Facing

(1) Oxidant transport and pollutant accessibility

This represents the most fundamental technical bottleneck faced by ISCO. The

distribution of contaminants in subsurface environments is highly heterogeneous; certain pollutants are trapped within low-permeability matrices (e.g., clay lenses and silt layers) or within the microporous structures of soil organic matter, making it difficult for oxidant molecules to diffuse into these "dead ends." The high degradation rates observed under laboratory conditions are typically based on the ideal mixing assumption; in actual field settings, the effective contact ratio between oxidants and pollutants is far below 100%. Modeling studies have shown that even when the stoichiometric ratio of oxidants is sufficient or even excessive, contact limitations alone can lead to the "survival" of 20%–40% of the pollutants [45].

(2) Secondary Pollution and By-products

Whether chemical oxidation can "become increasingly toxic" remains a subject of ongoing debate. Key concerns include: (1) intermediate products generated during incomplete oxidation may exhibit higher toxicity than the parent compound (e.g.intermediate products from Fenton oxidation of trichloroethylene include dichloroacetic acid and other known carcinogens); (2) the precipitation of Mn^{2+} and MnO_2 during $KMnO_4$ treatment; and (3) the generation of large amounts of SO_4^{2-} by activated persulfates—although this byproduct is less toxic, it may alter the mineralization level and corrosivity of groundwater [46]. Additionally, chemical oxidation inherently constitutes a "chemical sterilization" process, and the recovery period of soil ecological functions post-treatment warrants careful consideration.

(3) Uncertainty in the evaluation of restoration outcomes

The effectiveness of chemical oxidation is typically evaluated using the "decrease in pollutant concentration" criterion; however, a decrease in concentration does not equate to the elimination of risk. (a) The "rebound" issue: during remediation, pollutant concentrations drop significantly, but after cessation of injection, slow release of NAPL phases or highly adsorbed pollutants can lead to a rebound in concentrations; (b) The "insufficient characterization of toxicity" issue: concentrations of target pollutants decrease, yet the toxicity of their degradation products remains unknown; (c) The "sampling representativeness" issue: the heterogeneity of soil means that limited sampling points may fail to comprehensively reflect remediation outcomes [47]. These uncertainties create technical ambiguities in determining the remediation objective—specifically, "to what extent should remediation be achieved to be considered safe?"

6.2. Future Development Trends

(1) Intelligent and Precise Oxidation

By integrating high-precision site characterization techniques—such as membrane interface probes (MIP) and laser-induced fluorescence (LIF) for real-time monitoring—with numerical simulations (e.g.,), reactive solute transport models), it is possible to achieve "on-demand allocation" of oxidants: precisely targeting high-concentration regions for localized delivery rather than uniform injection. This

approach represents a promising direction for enhancing oxidant utilization efficiency. Furthermore, the application of machine learning in oxidant formulation optimization, injection parameter design, and remediation effect prediction has also garnered increasing attention [48].

(2) Novel oxide materials

The development of nanoscale oxidizing materials has become a prominent research focus. The activation of persulfate systems by nanoscale zero-valent iron (nZVI) leverages both the reduction and dehalogenation capabilities of nZVI and the oxidative capacity of SO_4^{2-}, enabling dual "reduction + oxidation" remediation. Metal-organic frameworks (MOFs), serving as heterogeneous catalysts for persulfate, exhibit outstanding catalytic activity and recyclability. Calcium peroxide (CaO_2) nanoparticles, functioning as a "solid-phase H_2O_2 slow-release source," can continuously release H_2O_2 over several weeks, thereby overcoming the drawback of rapid depletion following a single injection of liquid H_2O_2 [49].

(3) Chemical-Biological Combined Remediation

Chemical oxidation and bioremediation are no longer regarded as mutually exclusive approaches, but rather as complementary strategies. The sequential remediation strategy of "chemical pretreatment followed by biological refinement" is gaining increasing recognition: first, chemical oxidation is employed to rapidly reduce the concentration of the primary pollutants in high-concentration contaminated sites, lowering their levels to a range tolerable for biodegradation (thereby avoiding the toxic inhibition of microorganisms caused by high pollutant concentrations); subsequently, the metabolic activity of native or engineered microorganisms is leveraged to achieve sustained, low-cost "refinement" and ecological restoration [50].

(4) Green and Sustainable Restoration Philosophy

The traditional remediation paradigm, which prioritized meeting regulatory standards as its sole objective, is evolving toward a "Green and Sustainable Remediation" (GSR) approach. GSR requires a comprehensive evaluation of four key dimensions in remediation decision-making: environmental benefits (removal of pollutants), environmental footprint (carbon emissions and energy consumption associated with chemical agent production, transportation, and application), social impacts (disruption to community life), and economic costs [51]. Under this framework, the conventional mindset—that "the greater the dosage of chemical oxidation, the better" and that "the faster the remediation rate, the better"—is being supplanted by a more prudent principle: "using only what is necessary."

7. Conclusions and Outlook

Over the past three decades, chemical oxidation remediation technology has evolved from initial laboratory chemical experiments to becoming one of the cornerstone technologies for the remediation of organic-contaminated sites. Using the VOC

contamination at the former pesticide plant in Hangzhou as a case study, this paper systematically reviews the technical framework of this technology, the characteristics of its primary oxidation systems, key influencing factors, and advancements in engineering practice. The key insights can be summarized as follows:

First, each of the three mainstream oxidation systems possesses a unique and irreplaceable technical positioning. The Fenton reagent excels in its highly potent ·OH oxidizing capability and rapid reaction kinetics, making it particularly suitable for emergency remediation and rapid reduction of high-concentration pollutants; activated persulfate leverages the sustained transport of SO_4^{-}· and its broad-spectrum applicability, establishing it as the prevailing technical approach in ISCO applications; potassium permanganate is characterized by high selectivity, a non-radical direct oxidation mechanism, and excellent subsurface persistence, rendering it irreplaceable in the treatment of chlorinated hydrocarbons containing unsaturated bonds. No universal "optimal oxidant" exists; selection should be guided by the principle of compatibility between site-specific conditions and the target pollutants.

Second, soil properties, particularly organic matter content, pH buffering capacity, and permeability heterogeneity are the primary factors influencing the actual effectiveness of chemical oxidation; their importance may even surpass that of the chemical properties of the oxidizing agent itself. The extrapolation of laboratory-scale pilot test data to engineering scales must be grounded in comprehensive field characterization data.

Third, the limitations of chemical oxidation must also be duly acknowledged: the conflict between oxidant transport and pollutant accessibility, the toxicological uncertainties of degradation products, and the multidimensional challenges in assessing remediation efficacy, all of which constitute current bottlenecks hindering the further development of this technology.

Looking ahead, chemical oxidation remediation is evolving toward becoming "smarter" (precise injection), "greener" (reducing carbon footprint and secondary impacts), and "more synergistic" (seamlessly integrating with biological remediation, monitoring natural attenuation, and other approaches). For China, the numerous contaminated sites emerging during large-scale urban renewal initiatives present both challenges and opportunities that remediation practices at the Hangzhou pesticide plant and similar cases are accumulating distinctive Chinese experience in this technological field.

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