Development of VCHs Transfer Mechanism and Remediation Technology in Contaminated Sites

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Abstract. In recent years, with the adjustment of China's economic structure and the acceleration of urbanization, a large number of heavily polluting enterprises are facing shutdown and relocation, the residual volatile chlorinated hydrocarbons (VCHs) in the site become the priority pollutants in soil and groundwater due to the great threat to human body and environment. How to accurately predict the occurrence state and pollution degree of VCHs in the polluted site and put forward reasonable and targeted effective prevention and control strategy has become an international problem to be solved. The remediation technology of volatile chlorinated hydrocarbons (VCHs) in contaminated sites is introduced systematically, which will provide scientific basis for the practical remediation of contaminated sites in the future.

1. Introduction

Soil, as an important part of the environment and ecosystem, is the repository of biogeochemical circulation of matter, and is also an important resource for human survival [1]. With the rapid advancement of China's industrialization process, a large number of industrial waste water, waste gas, waste residue without any treatment directly discharged, causing serious environmental pollution. China's per capita land area is only one third of the world average. Affected by geographical location and topographic characteristics, the quality of land resources in China is generally not high [2]. At the same time, with the rapid growth of China's population and the rapid development of industry, land, a necessary resource for human beings, is under more and more pressure, and soil pollution has attracted much attention [3].

According to “Bulletin of the national survey on soil pollution” in 2014, the overall state of the soil environment is not optimistic, and the total rate of soil exceeding the standard is 16.1%. Among the 2,523 soil points in 146 industrial parks surveyed, the excess points accounted for 29.4%. The main pollutants in and around the metal smelting industrial park are Cd, Pb, Cu, As and Zn, and the main pollutants in the chemical park and surrounding soil are polycyclic aromatic hydrocarbons (PAH) and other volatile chlorinated hydrocarbons (VCHs). VCHs has stable chemical properties, low boiling point, high density, and is insoluble in water [4]. Once it enters the environment, it has stronger migration and infiltration performance, which will cause a large area of site pollution. If not timely management, it will produce many adverse effects on the regional ecological environment. So
countries have successively formulated relevant policies to clarify VCHs pollution investigation, assessment and pollution remediation and other relevant liability system and related soil environmental quality standards, such as the "superfund law" of United States and “Soil pollution prevention and control law” of Japan [7-9].

However, China has no specific legislation on VCHs pollution, and relevant laws and regulations are only general provisions for soil monitoring, and the base value is much higher than that of the United States and other developed countries. In terms of technology, a large number of remediation studies on contaminated sites have been conducted since the 1980s, and a series of remediation technologies for VCHs contaminated soils have been developed, such as vacuum extraction, bioremediation, multiphase extraction and thermal desorption technologies [10].

2. Research status of repair technology at home and abroad
From the 1980s, a large number of contaminated site remediation studies were carried out abroad, and a series of VCHs remediation technologies were developed [11, 12]. According to whether the soil position changes or not, the remediation technology of contaminated soil can be divided into in-situ remediation and ex-situ remediation [11]. The most applied technique are: (1) In-situ restoration: Soil Vapor Extraction (SVE), Bioremediation, Multi-phase Extraction, Solidification / Stabilization (S / S). (2) Ex-situ restoration: Solidification / Stabilization (S / S), Thermal Desorption and bioremediation [13].

2.1. Soil vapor extraction
Soil vapor extraction is one of the most economical and effective techniques for remediation of soil contaminated by VCHs. It uses the pressure gradient through the extraction well attract unsaturated zone soil air in order to reduce the vapor pressure in the soil pore, and uses gas flow promotes the evaporation of liquid pollutants in the soil, to speed up the volatilization of dissolved pore water pollutants, accelerate soil adsorption state of pollutants desorption, and thus increase the pull gas VCHs gas concentrations in the unsaturated zone, and then exhaust the extracted gas or liquid after harmless treatment to achieve the goal of repair [12].

However, the purification efficiency of SVE system is restricted by many factors [14, 15], including: (1) physical and chemical properties of pollutants; (2) characteristics of soil unsaturated zone. Among them, the volatility of pollutants and soil air permeability are the most important factors affecting SVE, often determining the design and operating efficiency of SVE system [16]. Understanding the adsorption, desorption, volatilization and diffusion of VCHs pollutants in soil plays a crucial role in the design of SVE systems, optimization of extraction conditions or operation processes, and timely shutdown of SVE systems.

2.2. Bioremediation
Bioremediation technology refers to the use of organisms, biological metabolic reaction process or biosynthesis products for the treatment and remediation of contaminated soil [17]. Bioremediation of contaminated soil refers to the process of comprehensive application of modern biotechnology to remove harmful pollutants from soil and improve or improve soil quality, including microbial, plant, animal and enzyme remediation methods [18]. Enzymes released into the environment by plants can degrade organic pollutants that are difficult for bacteria to degrade, such as TNT, trichloroethylene, PAHs and PCB [19, 20].

However, sometimes microbial remediation cannot remove all pollutants in the soil, and the complete remediation of contaminated soil can only be achieved when a unified treatment technology system is formed with physical and chemical treatment methods. Therefore, how to improve the efficiency of microbial repair is one of the hot topics in this field [21].
2.3. Solidification/Stabilization

Solidification/stabilization technology is through the physical and chemical methods to reduce the liquidity of harmful substances and pollutants in the environment [22, 23]. Solidification refers to the process of packaging waste materials in a solid product with high structural integrity. Stabilization is the process of reducing risk by converting a pollutant into a less soluble, stable, and less toxic waste. Vitrification is a typical solidification/stabilization technique that "melts" the soil at extremely high temperatures (1600 ~ 2000℃) and destroys organic pollutants through pyrolysis. In the process, most of the pollutants in the soil evaporate, while the rest are converted into chemically stable glass and crystal structures that are hard, durable and leach-resistant. Vitrification has a good effect on VOCs/SVOCs disposal, and the removal rate is above 90%. The depth of pollutants in the soil will limit the application of this technology, and long-term monitoring is needed to ensure the effective fixation of pollutants [24]. Therefore, how to realize online real-time monitoring has become a technical problem that still needs to be solved.

2.4. Thermal Desorption

Through direct or indirect heat exchange, thermal desorption technology heats organic pollutants in the soil to a sufficient temperature to evaporate or separate them from the contaminated soil. In the process of thermal desorption, evaporation, distillation, boiling, oxidation and pyrolysis occur. Some organic pollutants in the soil decompose at high temperature, but most of the undecomposed pollutants are separated from the soil into the flue gas, and then the polluted flue gas is purified [25, 26]. The main factors influencing the application and efficiency of thermal desorption technology include pollutant characteristics (pollutant types), equipment operation characteristics (heating temperature, residence time, contact degree between materials and heat sources) and soil characteristics (soil moisture content, soil texture and particle size, soil organic matter, etc.). When Fu haihui et al. [27] studied the thermal desorption characteristics of PBDEs in soil, they found that the total removal rate of PBDEs increased with the increase of particle size. Qi et al. studied the law of thermal desorption of PCBs in soil particles, and found that the removal rate of PCBs in fine particles (< 250m) was higher than that of coarse particles (420 ~ 841m). It was inferred that the diffusion rate of PCBs in the soil was a rate-limiting step that affected its removal rate, and PCBs in smaller particles were more likely to escape from the soil surface from the soil particles. The reasons for the inconsistencies in laboratory studies may be related to the concentration of pollutants in soil particles of different sizes [28], or may be due to the different physicochemical properties (organic matter content, soil mineral composition) of the soil.

Some studies have shown that the presence of soil organic matter can strengthen the binding force of pollutants and soil, thus inhibiting the thermal desorption process [27-30]. However, soil organic matter does not always inhibit the thermal desorption process of pollutants. Zhangyu studied the thermal desorption process of pollutants in three soils with different organic matter contents. This is because in the soil with high organic matter content, the heat loss of organic matter in the process of thermal desorption is significantly increased, so that the pollutants adsorbed on these organic matters are released, thus improving the removal rate of pollutants. In addition, the content of organic matter in soil not only affects the desorption process of pollutants, but also affects the selection of thermal desorption technology forms. In a word, the systematic study on the migration and transformation of VCHs in the site will effectively promote the further development and application of thermal desorption technology.

3. Migration and transformation of VCHs

The lack of theory limits the development of VCHs contaminated site remediation and treatment technology. At present, the research on VCHs migration and transformation process at home and abroad mainly focuses on adsorption and biodegradation. On the basis of a large number of adsorption-desorption characteristics and mechanism, some research results of process mechanism and kinetic model have been obtained. In theory, pollutants in underground environment generally exist in
soil and groundwater at the same time, and the equilibrium process of adsorption and desorption occurs at the interface of the two. Compared with a large number of studies on organic pollution in unsaturated zones, the study on organic pollution in groundwater is still in its infancy, and the research on migration, transformation and remediation mechanism of organic pollutants is still immature.

3.1. Migration and transformation law of vadose zone

In recent years, the organic pollution of groundwater has become a hotspot of groundwater science, and has been widely concerned. As the only way for pollutants to enter groundwater, the organic pollution of groundwater in the gas-encasement zone has been paid more and more attention. Gas belt pollution will not only cause groundwater pollution, but also bring great harm to human and biology. Therefore, research on the migration and transformation of pollutants in the gas belt and pollution treatment can further prevent groundwater pollution. There are a lot of research results abroad on the multi-phase and multi-component, 1-d and 2-d laboratory experiments of organic pollutants in the gas-encased zone, which lays a foundation for determining the migration and transformation law of pollutants in the gas-encased zone. There are few researches on the migration mechanism of multiphase flow in China, especially the research on the compound pollution in the gas belt is just at the beginning, which needs further work.

The migration and distribution of organic pollutants in the zone are controlled by many factors, such as physical and chemical properties, soil properties, etc. It mainly migrates along the vertical direction, so the migration model is usually treated as the vertical one-dimensional problem. When considering only dispersion, degradation and adsorption, given initial conditions and boundary conditions, the spatial and temporal distribution of pollutant concentration in the gas-enveloped zone can be determined by establishing the basic equation of vertical migration. However, the above model is difficult to solve the multiphase flow problem. A centrifugal model was used to study the migration of organic pollutants in the gas entrainment zone. The model can not only simulate the stress level of soil, but also reduce the model size, shorten the test time, and establish various heterogeneous models. In the study on VCHs pollution in a plain area carried out by Daniel Romen et al., it was shown that the equilibrium relationship between the gas and liquid phases of organic matter in the soil follows Henry's law, and the concentration of VCHs increases with the decrease of the distance to the interface. Martine Bohy et al. studied the migration and transformation law of trichloroethylene in the encapsulation zone by using 25m×12m×3m artificial encapsulation zone experiment and numerical simulation method, and compared and analyzed the test results and numerical simulation results. They believed that the temperature and gas-liquid equilibrium relationship was an important factor affecting the migration and transformation mechanism of trichloroethylene in the encapsulation zone.

3.2. Migration and transformation law of saturated zone

VCHs adsorption in the soil of small, big density, low viscosity, volatile, resulting from the surface into the soil under the action of gravity down penetration, mobility is very strong, often in several meters underground formation pollution and dozens of meters away from the center, if not handled in time, move will eventually spread to aquifer groundwater pollution. Up to now, the organic pollution of groundwater is still the most common and the most difficult to treat, which has attracted the attention of governments. Existing studies show that the migration and transformation of chlorinated organic compounds in groundwater mainly include adsorption / desorption, convection migration, dispersion / diffusion and natural attenuation, etc., which affect the final trend and final form of pollutants in groundwater. Generally speaking, the flow direction and velocity of pollutant migration depend on the flow field and velocity of groundwater, dispersion affects the diffusion of pollutants in the horizontal and horizontal directions of the flow field, adsorption and desorption block the migration of pollutants, and biodegradation determines the final destination and product form of pollutants. These effects are related to the physical and chemical properties of pollutants, aquifer properties and groundwater recharge, which together restrict the behavior of pollutants in soil and groundwater. Because there are many factors affecting pollutant migration and transformation, people
prefer to use mathematical model to simulate the actual situation and discuss the migration and transformation law in groundwater.

Cong Kaixiao using GMS software to typical pollution area to simulate area of chlorinated hydrocarbons, trichloroethylene and tetrachloroethylene as simulation object, based on water flow model the solute model, simulation and analysis of the transition and transform rule of chlorinated hydrocarbons in groundwater, and found that the degradation of tetrachloroethylene and trichloroethylene mainly related to the REDOX environment. In the model, the retardation coefficients of tetrachloroethylene and trichloroethylene are not different from each other in groundwater, which are 6.52 and 6.34 respectively. Lu qiang by tracking monitoring of groundwater in the area of chlorinated hydrocarbons (CAHs) fat content and environmental factors, it is concluded that CAHs natural attenuation coefficient, and then according to the hydrogeological conditions, using the Visual MODFLOW software simulation situation for a long time, CAHs in groundwater pollution plume migration, to provide the accurate range for subsequent groundwater restoration.

4. Prospect of soil VCHs remediation technology
   (1) The soil pollution ground repair, in the first step in our country, various law standard is not perfect, repair technology in theory is more laboratory studies, less actual engineering experience, this needs the government and social support of soil pollution prevention and control of repair technology research, establish a soil remediation technology application specification management policy, financing mechanism and legislation.
   (2) Due to the complex migration and transformation law of VCHs in the soil and underground water layer of the site, the pollution range of VCHs in the contaminated site cannot be accurately obtained. Therefore, it is necessary to establish scientific and reasonable pollutant migration and diffusion simulation software, which can be combined with remediation technology to realize scientific remediation.
   (3) The soil pollutants in the contaminated sites do not exist in a single or isolated state. In many cases, they are compound pollution caused by organic compounds and heavy metals, heavy metals and heavy metals. Due to the complex mechanism of compound pollution, the remediation method will be different from the traditional single remediation method. The actual situation is to consider the efficiency, thoroughness and economy of repair technology, and choose one or several joint best repair technology.

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