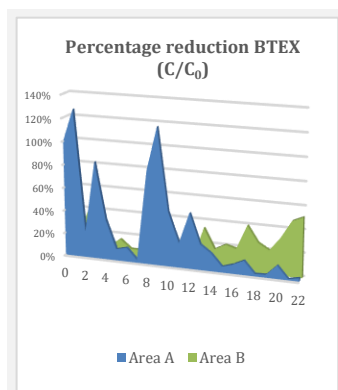


Challenges of using Ozone Sparging for in-situ chemical oxidation in BTEX contaminated areas

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This study investigated the performance of the ozone sparging technique in the remediation of areas contaminated by BTEX. To this end, the results of two pilot tests conducted in hydrogeologically similar areas, but with different levels of contamination, both in dissolved and retained phases, were evaluated. The results indicated that for areas with dissolved phase contamination and soil with low organic matter content, ozone sparging is highly efficient in reducing BTEX concentrations to acceptable levels. However, in areas with retained phase contamination in soil rich in organic matter, the performance of ozone sparging is significantly affected, making it an economically unviable technique for initiating remediation in such areas. Nevertheless, when combined with other techniques or used as a polishing step, it proves to be a highly efficient solution.

Introduction

Soil and groundwater contamination by volatile organic compounds (VOCs) poses a critical environmental challenge for contemporary society. Beyond requiring restrictions on groundwater use, these contaminated areas pose serious risks to human health and the environment. To address this issue, various remediation technologies have been developed, with In Situ Chemical Oxidation (ISCO) being one of them. ISCO remediations can be implemented using different types of oxidants, each with its own advantages and limitations. Among these oxidants, ozone stands out as an option, being injected into the aquifer in gaseous form along with compressed air, in a process known as ozone sparging. The advantages of this oxidant lie in the fact that it is produced on-site and does not generate by-products after oxidation, making it a more sustainable option compared to other oxidants. Additionally, ozone sparging can promote other remediation processes that act synergistically with oxidation, such as the volatilization of VOCs and, secondarily, aerobic degradation due to the increased dissolved oxygen in groundwater.

However, the application of this oxidant faces a series of practical challenges that need to be considered to evaluate its technical feasibility, such as the low mass transfer efficiency of gaseous ozone to the liquid phase, its high instability which causes it to degrade into oxygen within minutes, and the hydraulic difficulty of distributing a gaseous fluid in a porous medium. Other aspects, such as high concentrations of oxidizable substances and organic matter present in soil and water, require a larger mass of ozone to be injected into the aquifer to achieve remediation objectives.

In this context, this study aims to evaluate the performance of two ozone sparging pilot tests for the remediation of BTEX. These tests were conducted in hydrogeologically similar areas, but with different

levels of contamination. In one area, contamination was present in both groundwater and soil (presence of a secondary source), while in the other area, contamination was present only in water at concentrations 100 times lower.

Material and Methods

The areas selected for the tests (Area A and Area B) are close, approximately 400 meters apart, with an average water table depth of 1 meter. The geology and hydrogeology are common to both areas, consisting of the first meter of silty landfill, followed by a layer of sand (flow zone) with a variable thickness between 3 and 5 meters. Below the sand, there is a thin layer of organic clay (between 0.2 and 0.5 meters), and below this clay, a layer of marine clay.

The contaminants present in both areas are BTEX, with benzene being the major compound. In Area A, groundwater concentrations of this substance were quantified at around 100 µg/L. In the soil, both in the sand layer and in the clay layers, VOC concentrations were not quantified. In Area B, benzene concentrations in groundwater were two orders of magnitude higher than those found in Area A. In the soil of this area, benzene concentrations were quantified in the transition from the sand layer to the organic clay/marine clay layer.

The tests were conducted with the installation of 5 wells for injecting the ozone-compressed air mixture in each area, as well as observation wells to monitor the remediation process. The wells used for injection were installed with fine bubble diffusers, with a maximum length of 50 cm. In Area A, the diffusers were positioned in the sand, just above the organic clay layer. In Area B, the diffusers were positioned in the sand layer, but partially penetrating the organic and/or marine clay.

The ozone used in the tests was generated by the corona principle, with a generator shared for both

areas and with a capacity of 60 g/h of ozone. The tests lasted 35 weeks in Area A and 28 weeks in Area B. It should be noted that injection pressures and flow rates were adjusted daily to maintain the same conditions for these variables in both areas. To monitor the environmental evolution, weekly groundwater samples were collected from observation wells and sent for BTEX analysis in the laboratory. Additionally, physical-chemical parameters (dissolved oxygen, redox potential, pH, electrical conductivity, and temperature) of groundwater were monitored twice a week, also through the observation wells.

Results and Discussions

In total, approximately 100 kg of gaseous ozone was generated and injected into the aquifer in each area. However, it should be noted that not all of this mass dissolves in water, as only a fraction of the injected amount will act in the oxidation of the target chemical compounds.

The pilot test results revealed distinct performances between the two studied areas. In Area A, characterized by a lower initial concentration of BTEX and diffusers positioned in the sand, an increase in redox potential accompanied by an increase in dissolved oxygen was observed after 4 weeks from the start of the test. Regarding BTEX concentrations, at the end of the test, the observation wells showed analytical results below the laboratory's quantification limit, resulting in a 100% reduction in BTEX concentrations. Additionally, post-shutdown monitoring of ozone sparging did not indicate a return of the target contaminants' concentrations (rebound effect).

In Area B, characterized by higher BTEX

concentrations than in Area A and with diffusers partially positioned in sand and partially in organic and/or marine clay layer, a different behavior from Area A was observed. BTEX values showed a median reduction of about 87% in the first week of the test. However, this reduction was not accompanied by an increase in redox potential data, nor by an increase in the median dissolved oxygen. Only in the 16th week was it possible to observe a general increase in redox potential in the area. It should be noted that during this same period, BTEX concentrations showed a trend of increase, and at the end of the test, the median BTEX concentrations were higher than the median of the first week, representing a reduction of about 40% relative to the baseline. It is noteworthy that this reduction did not reflect concentrations below the CONAMA 420 guideline values.

The performance of ozone sparging in Area B, inferior to that in Area A, is related to the position of the ozone diffusers and the mass of BTEX retained in the soil matrix. These conditions suggest that ozone entering the aquifer was consumed more rapidly by the organic matter in the clay layer, which may explain the observed behavior for redox potential and dissolved oxygen.

Thus, the significant drop in BTEX concentrations in the first week of the test was more influenced by the sparging effect of the gas fluid (volatilization) than by ozone oxidation. The rebound effect observed over the course of the test is related to the presence of contaminants in the retained phase in the soil matrix. Ozone sparging disrupted the aquifer's chemical equilibrium, promoting the release, via reverse diffusion, of BTEX mass sorbed in the soil matrix to the dissolved phase in the water matrix.

Conclusions

The results obtained for the performance of ozone sparging in the two studied areas suggest that this remediation process is highly efficient for areas with dissolved phase concentrations and low organic matter content in the soil. Conversely, in areas where, in addition to the dissolved phase, there is contamination in the retained phase and soil rich in organic matter, ozone sparging has lower efficiency. In this situation, the main pathway for reducing contaminant concentrations occurs through volatilization, making this technique economically unappealing as an initial or sole remediation process for the area. However, ozone sparging can be combined with other techniques or used in a more advanced stage of area remediation as an efficient polishing method.

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