

Combination of In Situ Chemical Oxidation with In Situ Solidification for Treatment of Contaminated Areas

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In situ chemical oxidation (ISCO) and in situ soil solidification (ISS) are established technologies for remediating contaminated areas. By combining them, it's possible to maximize their individual benefits. Typically used in contaminated soils, this study proposes a new challenge by evaluating ISCO-ISS remediation in sediments. For this purpose, the results of a bench-scale test employing the ISCO-ISS combination to treat sediments contaminated with metals, VOCs, and SVOCs were analyzed, confirming that this combination is a viable remediation alternative. It was observed that the alkalinity of the Portland cement activated the persulfate, resulting in significant reductions of VOCs (between 51.6% and 59.5%) and SVOCs (between 80.5% and 85.2%). Additionally, there was a decrease in contaminant concentrations in leachates, evidencing the synergistic effects of this approach.

Introduction

In situ chemical oxidation (ISCO) and in situ soil solidification (ISS) are two distinct and well-established technologies for remediating contaminated areas. The former uses oxidants such as sodium persulfate to promote oxidation and consequently destroy mass of contaminants in the aquifer. The latter aims to reduce the mobility and solubility of contaminants in the soil to be remediated, also reducing hydraulic conductivity and increasing soil compression resistance.

The combination of these two technologies is an innovative approach and produces effects that enhance the positive aspects of each technique. The alkalinity of Portland cement, used in the soil solidification process, is used to create pH conditions that activate sodium persulfate, forming powerful oxidizing radicals such as sulfate and hydroxyl radicals. These, in turn, promote the oxidation of contaminants while the solidification process occurs. At the end of this process, leaching of contaminants from the solidified soil to groundwater is reduced, compared to using ISS alone.

ISCO-ISS processes are typically performed in contaminated soil; however, this study proposes a new challenge by evaluating ISCO-ISS remediation in contaminated sediments. Therefore, the aim of this study is to evaluate the results obtained in a bench-scale test to assess the applicability of ISCO-ISS in treating sediments contaminated with metals, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs) with different proportions of persulfate and Portland cement.

Material and Methods

For the bench-scale test, sediment samples (from a former deactivated effluent treatment pond) were collected from the contaminated site. These samples were homogenized and separated into bottles for the

test. However, to establish baseline values, an aliquot of this matrix was sent for analysis of metals, VOCs, SVOCs, pH, and moisture.

Subsequently, the bench-scale test was divided into three stages. The first stage consisted of compression strength tests, where the sediment was mixed with different proportions of oxidant and Portland cement, and its strength was measured using a penetrometer after 4, 14, and 28 days of mixing. In total, 20 different mixtures were evaluated, testing both domestically sourced and imported cement. It's noteworthy that the persulfate used in all stages of the bench test was Klozur® persulfate from Evonik.

Based on the results of stage 1, three persulfate and cement proportions were selected for the stage 2 tests. This stage aimed to evaluate the ability of Portland cement-activated persulfate to oxidize contaminants in the sediment under study. For this purpose, three samples of contaminated sediment were prepared with the selected proportions from stage 1, along with a control sample (contaminated soil without persulfate and cement), forming a set of 4 samples.

From each of these samples, aliquots were collected for analysis of VOCs, SVOCs, soil compression strength, and hydraulic conductivity. These analyses were performed after 28 days of mixing the sediment with the cement and persulfate proportions.

After removal of the aliquots, the remaining samples were placed in 2"x4" cylindrical molds for stage 3 of the test. In this stage, the leaching capacity of metals, VOCs, and SVOCs from the stabilized sediment when in contact with water was evaluated. Thus, the 2"x4" cylinders of different soil, cement, and persulfate mixtures were placed in a container containing deionized water, including the control sample.

Different contact times of the cylinder with deionized

water were tested, and for each of these times, the contact water was analyzed for metals, VOCs, and SVOCs. The first leaching/contact time was 1 day, followed by discarding the leachates and placing the cylinders immersed again with deionized water, starting the second contact time, which lasted 1 day (or 2 accumulated days). In total, 5 leaching times were tested, being 1, 1, 5, 7, and 14 days. Considering accumulated days, they were 1, 2, 7, 14, 28 days.

Results and Discussion

The results of stage 1 showed that the compression strength of the sediment varied significantly depending on the proportions of persulfate and cement, with values ranging from 1.24 psi to 64 psi. These results helped define the following sodium persulfate (SP) and Portland cement (PC) proportions to be used in stage 2: sample 1 with 2% SP and 30% PC, sample 2 with 4% SP and 20% PC, sample 3 with 4% SP and 30% PC, and control sample without SP and PC.

The compression tests performed for these samples indicated values ranging from 5 to 30 psi. Generally, a compression strength between 30 and 60 psi is commonly considered for stable soil. Therefore, this value was also used as a reference for sediments. In this sense, only the result of sample 3 met this recommendation after 28 days. It is also noteworthy that the residual sulfate resulting from the decomposition of persulfate delays the solidification process. For hydraulic conductivity measured in stage 2, the values obtained after 28 days resulted

in hydraulic conductivities lower than 10^{-6} cm/sec, which are considered good results.

Regarding the mass destruction capacity of VOCs and SVOCs, measured in stage 2, it was found that compared to the control, VOC concentrations were reduced by 59.5% in sample 1, 51.6% in sample 2, and 52.8% in sample 3. For SVOCs, the results indicated a greater mass destruction, with a reduction of 83.1% in sample 1, 80.5% in sample 2, and 85.2% in sample 3.

Stage 3, which consisted of the leachate test, showed that the highest VOC, SVOC, and metal results were obtained in the leachate of the first contact day in all samples. These results are expected, since the surface of the test cylinders may contain contaminants that leach more quickly, resulting in higher values. For the other leaching times, the results indicated lower concentrations of metals, VOCs, and SVOCs, confirming that over time a lower mass flux rate of stabilized sediment to water is observed. It is noteworthy that sample 3 was the sample that produced leachates with the lowest concentrations of metals, VOCs, and SVOCs in all sampled times.

In a real field application, it is expected that the leachate flow to the surrounding water decreases until it reaches a diffusion limitation. As the surface area/volume ratio of the cylinders is greater when compared to actual field conditions, it can be assumed that the general trend of bench results is reproduced in the field, but the leachate values should be different.

Conclusions

The results of the bench test confirmed that the combination of ISCO with ISS is a viable alternative for treating contaminated sediments from the study site. The synergistic effects associated with the activation of persulfate by Portland cement were observed, as the treated sediments showed reductions in VOCs between 51.6% and 59.5%, and SVOCs ranging from 80.5% to 85.2%. Another effect observed was the reduction in contaminant concentrations in leachates, with sample 3 showing the lowest concentrations. This result is consistent with the compression strength value of this sample, which was the highest among the three tested samples. For samples 1 and 2, the compression strength did not reach values considered adequate because, unlike a conventional test using soil, this test used sediment. It is also worth noting that residual sulfate delays the solidification process, requiring a longer time to achieve higher compression strength. Based on the overall results, it can be concluded that sample 3 demonstrated the highest performance among the tested sediments.

Acknowledgments

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References

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