Ozone Injection in Soil Contaminated with Organic Compounds and Ions of Interest Evaluation

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Abstract *– In this study, field activities was carried out to collect soil and groundwater samples followed by laboratory work aiming at the hydro geochemical characterization of the unconfined aquifer. Studies led to experimental laboratory activities involving ozone injection through soil columns to detect and quantify the metal ions of interest that are mobilized from the solid matrix. Based on the study of the ion mobilization mechanisms resulting from remediation with ozone, it was possible to determine the ionic concentrations increase in groundwater. Experiment results confirmed that ozone injection in subsurized released pollutant ions such as Al^{3+} and Fe^{3+} affecting drinking water local standards. Other pollutant metallic ions of interest such as Cr^{2+}, Ni^{2+} and Pb^{2+} didn't demand ozone and were not mobilized because they were found as part of the crystalline structure, not being adsorbed on the surface of the grain and also not having been detected in the interstitial solution.*

Keywords: ozone, groundwater, soil, remediation, metal ions, oxy reduction

1. Introduction

Ozone is a highly reactive, unstable gas being a strong, non-selective oxidizing agent that reacts in both aqueous and gaseous media. These reactions may be direct or indirect involving the formation of free radical intermediates, which also have the ability to oxidize relative to the compounds of interest. Thus, some contaminants may be more sensitive to direct reactions than to oxidation reactions from free radicals. Therefore, the most efficient reaction path is determined by the characteristics of the target contaminant and the characteristics of the geochemical composition of the aquifer formation. The three most critical parameters for the success of ozonation are permeability, organic matter content and oxidant demand [1]. During the injection of ozone in the saturated zone of the aquifer, the phenomena related to transport and mass transfer determine the behavior of the oxidant and directly influence the effectiveness of the project. Some interactions with the soil and groundwater can be productive with formation of free radicals that increase the rate of oxidation, while other reactions are non-productive, being possible to mention the consumption of the oxidant by species that are not targets of the remediation project. Several studies support evidences that the natural presence of metal oxides in soil promotes ozone catalysis [2]. The main proposals of this study were detecting and quantifying metal ions of interest that are mobilized from the solid matrix by the ozone injection process, studying mechanisms of ionic mobilization resulting from ozone remediation and to determine the ionic concentrations increase in groundwater.

2. Methodology

Field work scope included: soil drilling execution, monitoring wells installation, soil and groundwater sampling. After area characterization and the contamination conceptual model elaboration the experimental work was performed using soil samples selected from the saturated zone of a petroleum hydrocarbon contamination representative spot.

Ozone injection system used in the experiment consisted of a pressurized oxygen cylinder with a capacity of 190 $Kgf.cm^{-2}$ directly connected to an ozone generator with a constant nominal capacity of 5.0 $g.h^{-1}$. At the output of the ozone generator, a flow meter with a scale ranging from 0 to 50 $cc.min^{-1}$ was positioned to control the mass injection flow rate. According to the equipment specification, ozone rate produced by the generator varies in a way directly proportional to the electric current, so in order to generate 5 $g.h^{-1}$ of ozone, a current of 1 Ampere is required. It is emphasized that the

correlation above is only valid when using pure oxygen to be delivered at the generator's feed. Figure 1 presents the equipment arrangement for the gaseous ozone application.
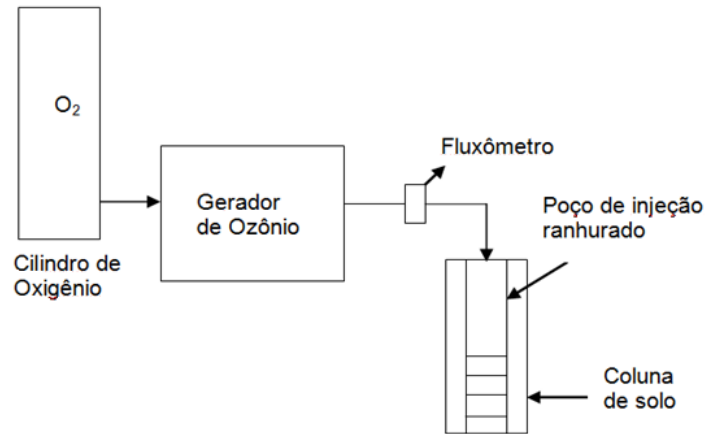

Fig. 1: Ozone injection system through soil column.

In order to ensure that chemical oxidation along the entire column was homogeneously performed during the experiment, filter section was repositioned 4 times in each column during the ozone injection period as presented in Figure 2.
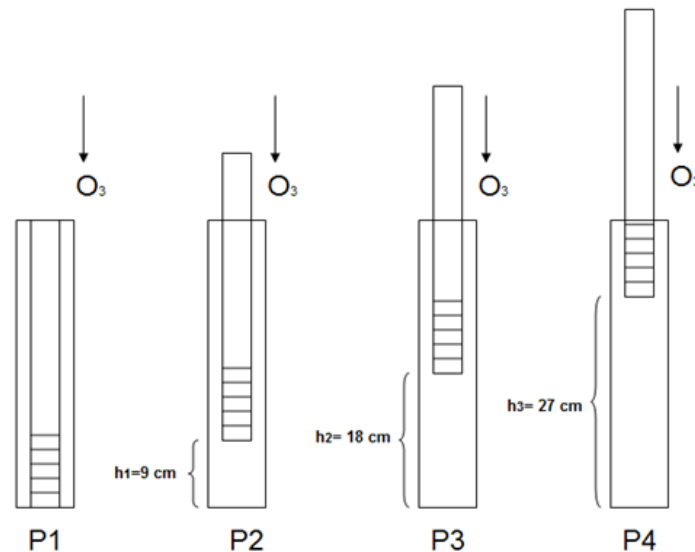

Fig. 2: Filter section repositioning.

Sample taken from Column 0 was not submitted to ozone injection. Each of the other 4 columns were ozonated for different periods of time as showed in Table 1. Soil remaining from each column was treated generating 5 soil samples that were submitted to mineralogical analysis, chemical analyses, pH, cationic exchange capacity, nitric and aqueous extractions.

Table 1: Ozonation period versus filter section repositioning.

Column	Ozonation Total Time (min)	Ozonation Time (min) - Postion P1	Ozonation Time (min) - Position P2	Ozonation Time (min) - Posição P3	Ozonation Time (min) - Position P4
1	10	2.5	2.5	2.5	2.5
2	20	5	5	5	5
3	30	7.5	7.5	7.5	7.5
4	40	10	10	10	10

Total ozonation entire period for this experiment was 100 minutes. It should be noted that at the end of the ozonation of each column the stainless steel tube used as an injection well was washed with water and neutral soap before being dried in an oven to avoid cross-contamination between columns.

3. Results and Discussions

In according with mineralogical analysis outcomes, X-Ray Diffraction has indicated the Gibbsite and Kaolinite presence, which characterizes a soil with low adsorption activity. Ozone didn´t affected any mineralogical soil parameter.

Soil samples were also submitted to chemical analysis to determine major and trace elements concentration. Considering this study proposal, main relevant major and trace elements detected were Al_2O_3, Fe_2O_3, MnO, Cr, Ni, Pb, Zn. Concentrations values for Cr, Ni, Pb and Zn were detected under the limits established for soil quality by the local regulatory agency.

Charges of the soil colloidal particles are determined by the values of ΔpH, calculated by the ratio $\Delta pH = pHCaCl_2 - pHKCl$. Analytical results showed positive values for ΔpH which indicates the predominance of negative charges capable to adsorb cations [3]. The Cationic Exchanging Capacity values at $pH = 7$ for all columns ranged from 23.94 to 25.96 $mmmolc.dm^{-3}$ corresponding to 2.4 to 2.6 $cmolc.dm^{-3}$. These results are considered low, confirming the predominance of clay 1:1 with low adsorption activity. These results are characteristic of tropical regions, where the soils are weathered, with predominance of clays with low adsorption power and low to medium organic matter content [4].

Results about the aqueous and nitric extractions were performed in order to quantify cations, respectively in the total (adsorbed + interstitial) and interstitial solutions, so the concentration of adsorbed cations could be determined by subtracting the nitric extraction results from the aqueous extraction results. Table 2 below consolidates the adsorbed cations concentration.

Table 2: Adsorbed cations ($mg.L^{-1}$).

	Adsorbed cations						
	Al^{3+}	Fe_{Total}	Mn^{2+}	Cr^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
Column 0	20.70	8.70	0.00	0.00	0.00	0.00	0.00
Column 1	25.00	9.90	0.00	0.00	0.00	0.00	0.03
Column 2	9.90	5.70	0.00	0.00	0.00	0.00	0.00
Column 3	17.20	7.30	0.00	0.00	0.00	0.00	0.00
Column 4	15.60	7.00	0.00	0.00	0.00	0.00	0.00

Results observed for nitric and aqueous extractions indicated that trace elements of interest are not adsorbed on the surface and not even present in the interstitial solution. Thus, although Cr^{2+} is susceptible to oxide-reduction reactions, the fact that it is not positioned on the clayey surface prevents it from being oxidized by the action of ozone applied to the soil during the experiment. Ni^{2+} and Pb^{2+} mobility depends exclusively on the pH variation and therefore do not demand ozone. Results had indicated that both are part of the crystalline structure, not being adsorbed on the surface of the grain and also not having been detected in the interstitial solution. The Zn^{2+} was detected punctually adsorbed and in solution in column 1, the zinc does not undergo oxidation-reduction reactions and therefore does not demand ozone. The concentrations detected are below the intervention value established by the regulatory agency for groundwater quality as 5.0 $mg.L^{-1}$.

For the major elements, the results of the nitric extractions indicated concentrations adsorbed to the clay minerals for Al^{3+} and Fe_{Total}. Mn^{2+} was not detected adsorbed and is also not part of the crystalline structure of the argillomineral, being present in the interstitial solution only. Although the oxidation reduction reactions are susceptible, the concentrations of Mn^{2+} in the interstitial solution remained constant, indicating that there was no interaction with the oxidizing agents due to ozone injection. According to the results, both Al^{3+} and Fe_{Total} showed a tendency of decreasing their concentrations of adsorbed cations on the clay minerals. Considering Fe_{Total}, the main mechanism responsible for its adsorbed concentration decreasing is the Fe_3 hydrolysis.

3.1. Calculation of the Adsorbed Maximum Concentration

Through a linear regression from the extrapolation of the line obtained by the projection of the adsorbed concentrations of the metal cation of interest as a function of the inverse of the square root of time, it is possible to determine the maximum concentration when the equilibrium of the remediation process is reached. It should be emphasized that the values referring to column 0 were excluded, since for time T = 0 it would imply a division by zero or a non-existent function.

The uncertainties were weighted from the coefficient of determination, also called R², which measures the degree of adjustment of a generalized linear statistical model, such as Linear Regression, in relation to the observed values. Values of R² ranges from 0 to 1, indicating, in percentage, how much the model explains the observed data, so the higher the R², the more explanatory is a model, because the better it fits the sample.

The results indicated an interval for the maximum concentrations in solution and in the colloid, after the moment that the reactions and mechanisms of ionic mobility ceased. Such an instant was determined by stabilization of the second decimal place of the concentrations in $mg.L_{-1}$. Figure 3 shows the corresponding analysis for Al_{+3}.
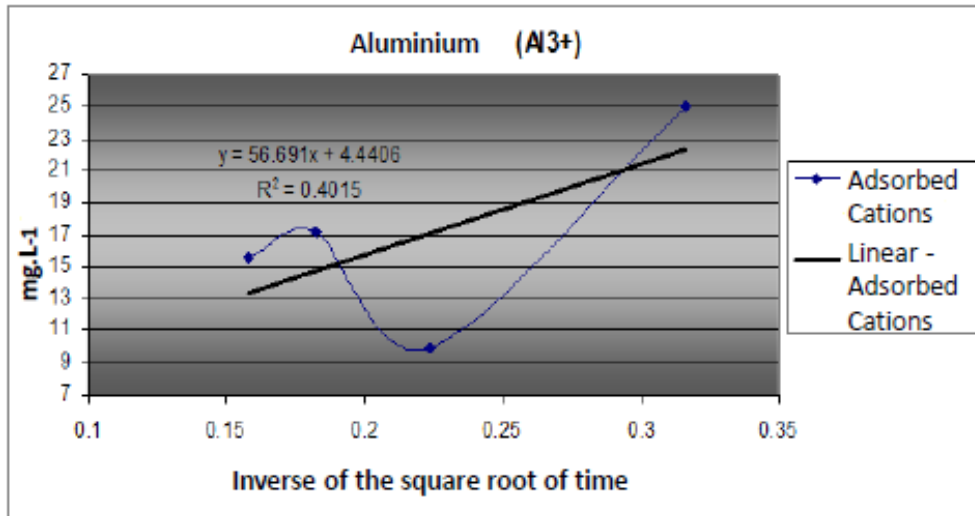

Fig. 3: Al^{3+} Adsorbed versus the inverse of the square root of time.

For the linear statistical model $R^2 = 0.4015$ was obtained, this means that 40.15% of the dependent variable can be explained by the regressors present in the model.

Figure 4 presents the extrapolation of the straight line obtained by the projection of Al^{3+} concentrations as a function of the inverse of the square root of time
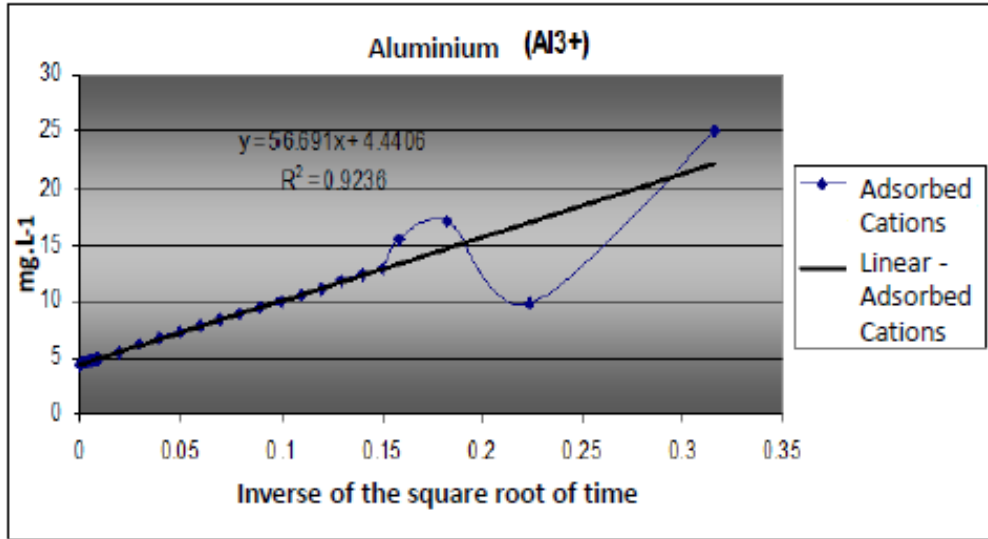
Fig 4: Al^{3+} maximum adsorbed concentration.

Maximum concentration of Al^{3+} adsorbed will be 4.44 mg.L^{-1}, it will stabilize at approximately 64000 minutes or 44 days. Considering that after 40 minutes of ozonisation, the detected concentration of adsorbed Al^{3+} was 15.6 mg.L^{-1}, and the lowest concentration to be reached was estimated at 4.44 mg.L^{-1}, it is possible to estimate that the concentration variation given by equation below will be added to the concentrations in interstitial solution.

$$\Delta[Al^{3+}]_{adsorbed} = 15.6 - 4.44 = 11.16 \text{ mg.L}^{-1} \tag{1}$$

After 40 minutes of ozonization the detected concentration of Al^{3+} in the interstitial solution was 4.0 mg.L^{-1}. Therefore the estimate for the maximum concentration to be observed in the interstitial solution is given by:

$$[Al^{3+}]_{interstitial} = 4.0 + 11.16 = 15.16 \text{ mg.L}^{-1} \tag{2}$$

Thus, it is possible to assume that the concentrations detected in the field for groundwater may have their value increased by up to 15.16 mg.L^{-1}.

Figure 5 presents the analysis performed for Fe_{Total}.
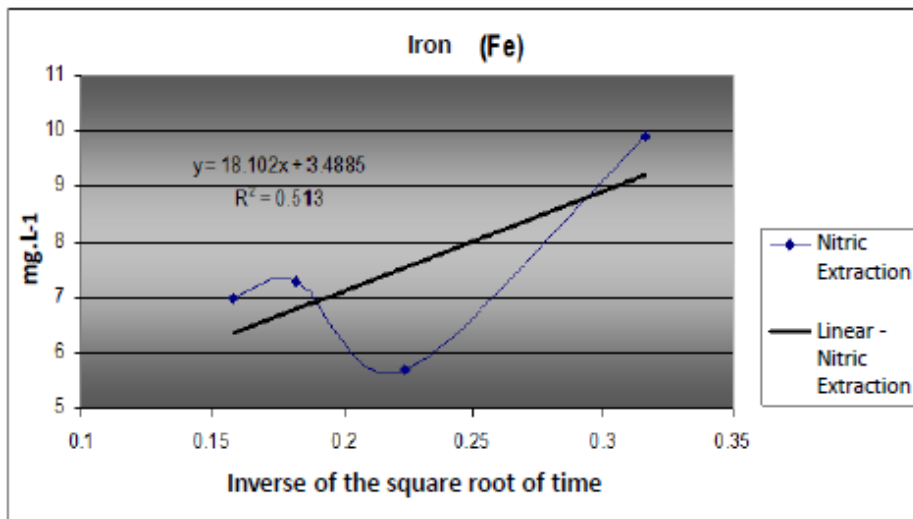

Fig 5: Fe_{Total} versus the inverse of the square root of the time.

For the linear statistical model $R^2 = 0.513$ was obtained, this means that 51.30% of the dependent variable can be explained by the regressors present in the model. Figure 6 presents the extrapolation of the straight line obtained by the projection of Fe_{Total} concentrations as a function of the inverse of the square root of time.
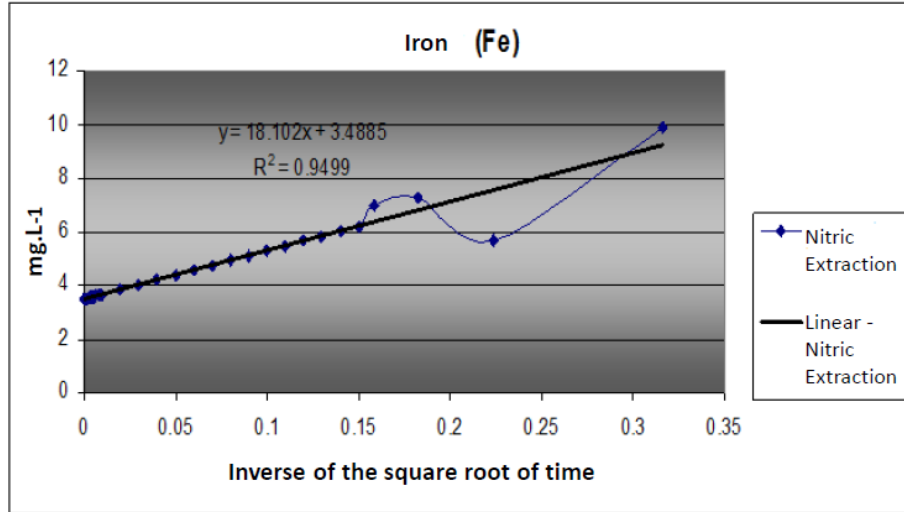

Fig 6: Fe_{Total} maximum adsorbed concentration.

The maximum concentration of Fe_{total} adsorbed will be 3.48 mg.L^{-1} and it will stabilize at approximately 80000 minutes or 55 days. Considering that after 40 minutes of ozonization the detected concentration of Fe_{total} adsorbed was 7.0 mg.L^{-1} and the lowest concentration to be reached was estimated at 3.48 mg.L^{-1}, it is possible to estimate that the adsorbed concentration variation, given by equation below, will be added to the concentrations in the interstitial solution.

$$\Delta[Fe_{Total}] = 7.0 - 3.48 = 3.52 \text{ mg.L}^{-1} \tag{3}$$

Fe_{Total} cation concentrations were not detected in the interstitial solution. Thus, it is possible to assume that the concentrations detected in the field for groundwater may have their value increased up to 3.52 mg.L^{-1}.

4. Conclusion

The application of the remediation technique by ozone injection may, depending on soil attributes, release pollutant ions such as Al^{3+} and Fe^{3+}, which may be available in the soil / O_3 system. Their levels decreased while the injection of O_3 time had increased. Al^{3+} concentrations adsorbed ranged from 20.7 mg.L^{-1} to 9.9 mg.L^{-1} while Al^{3+} concentrations in the interstitial solution ranged from 3.7 mg.L^{-1} to 4.0 mg.L^{-1}, all values above of the local regulatory agency standard for groundwater quality, settled at 0.2 mg.L^{-1} or 200 µg.L^{-1}.

Al^{3+} presence in solution indicates that the competition between H^+ cations, still present in the solution, and the adsorbed hydroxyl compounds ($[AlOH]^{2+}$; $[AlOH_2]^+$) causes its displacement from the precipitated layer because they are stable species in relation to the medium acidity.

The extrapolation of the line obtained by the Al^{3+} concentrations projection as a function of the inverse of the square root of the time indicated that, if the acidity conditions are maintained, the maximum concentration of Al^{3+} adsorbed will be 4.44 mg.L^{-1}, stabilizing in approximately 44 days. Thus, it was possible to infer that the concentrations detected in the field for groundwater may have their value increased by up to 15.16 mg.L^{-1}.

Adsorbed Fe_{Total} detected from the nitric and aqueous extractions presented concentrations from 5.70 to 9.90 mg.L^{-1}, above the limit established by the local regulatory agency for groundwater quality, which value is 0.3 mg.L^{-1} or 300 µg.L^{-1}. Extrapolation of the straight line obtained by the projection of Fe_{Total} concentrations as a function of the inverse of the square root of time indicated that, if acidity conditions were maintained, the maximum Fe_{total} concentration

adsorbed will be 3.48 mg.L^{-1}, stabilizing in approximately 55 days, it is possible to assume that the concentrations detected in the field for groundwater may have their value increased up to 3.52 mg.L^{-1}. Regarding Mn^{2+}, although it was susceptible to the reduction oxide reactions, its concentrations in the interstitial solution remained constant, indicating that there was no interaction with the oxidizing agents by the ozone injection.

Acknowledgements

References

[1]   ITRC (Interstate Technology & Regulatory Council). *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*, 2nd ed. ISCO-2.Washington, D.C.: Interstate Technology & Regulatory Council, In Situ Chemical Oxidation Team, 2005.

[2]   R. L. Siegrist, et al., *In Situ Chemical Oxidation for Groundwater Remediation*, doi: 10.1007/978-1-4419-7826-4_4, # Springer Science+Business Media, LLC 2011.

[3]   R. Hypolito, S. Andrade, S. Ezaki, *Geoquímica da interação: água, rocha, solo: estudos preliminares*. São Paulo: All Print Editora, 2011.

[4]   A. S. Lopes, L. R. G. Guilherme, "Interpretação de análise de solo – Conceitos e Aplicações," *Boletim Técnico nº 2. Associação Nacional para Difusão Adubos*, p. 36, 2004.