

The Effectiveness of Using Replacement Reactions of Carbonate Minerals in Removing Groundwater Pollutants

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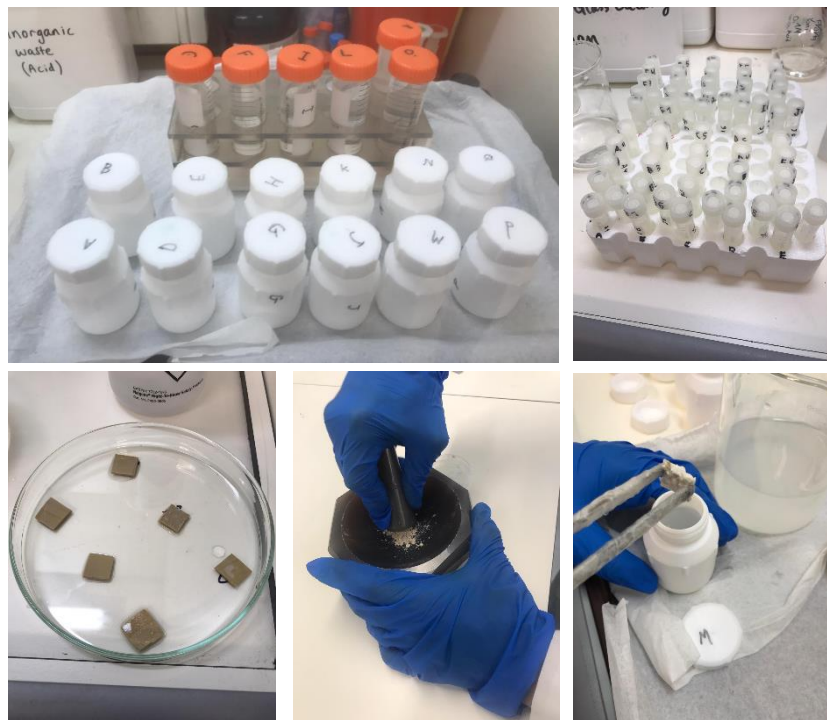


Table of Contents

Abstract	3
Introduction	4
Groundwater pollution	4
Treatment of contaminated groundwater.....	4
Replacement reactions.....	5
Oxalate and heavy metals.....	6
The research objective.....	6
Research Methods	7
Results	9
XRD	9
Elemental determination using ICP-MS.....	10
Pollutants that were removed by chemical replacement.....	11
Pollutants that were removed by chemical replacement and adsorption.....	12
Pollutants that showed no change in concentrations by chemical replacement and adsorption or direct precipitation.....	14
Discussion	15
The effects of calcite replacement reactions with oxalic acid in the presence of contaminants on aquifer rock	15
The effect of replacement reactions on the concentration of pollutants in the aquifer water	16
Conclusions	17
Bibliography.....	18
Appendices	19

1. Abstract

Heavy metals are a common groundwater pollutant, often due to natural processes and polluting human activity. Many important aquifers are dominated by limestone, a type of rock that comprises primarily of the mineral calcite (CaCO_3). Calcite may undergo a chemical reaction with oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) that results in its replacement to calcium oxalate (Ca-oxalate, $\text{CaC}_2\text{O}_4 \cdot (\text{H}_2\text{O})_x$, where x ranges between 0 and 3). It is known that a variety of metals such as zinc, lead, and cadmium may precipitate from solutions that are saturated with respect to Ca-oxalate. Furthermore, these poisonous metals may be incorporated into the mineral lattice during the replacement reaction of calcite into Ca-oxalate, which unlike calcite, is very insoluble. Thus, the replacement reaction of calcite into Ca-oxalate in the presence of heavy metals may trap these pollutants into the mineral lattice of Ca-oxalate, and thus remove them from the aquifer groundwater. This replacement reaction may contribute to the development of innovative methods for removing metals from aquifers dominated by carbonate rocks. However, the level of efficiency of the abovementioned replacement reaction in fixing heavy metals into the mineral lattice is not fully understood. To evaluate the efficiency of this reaction in removing pollutants, I carried out an experiment where I examined the reaction of carbonate rocks with oxalic acid in the presence of contaminants, where the extent to which the pollutants were incorporated into the solid minerals during the replacement reaction was determined. Through the characterization of the mineral composition of the solid phases using X-ray diffraction (XRD), I found that the replacement of limestone in the presence of oxalic acid does result in the desired replacement reaction. In addition, contaminant concentrations measurements using an inductively coupled plasma mass spectrometer (ICP-MS) demonstrated a decrease in the concentrations of several metals due to the replacement reaction. These results indicate that the replacement reaction of calcite into Ca-oxalate may be utilized for the removal of heavy metals from carbonate-dominated aquifers. Although the replacement reaction lowered the concentrations of certain heavy metals, the concentrations of other metals also diminished in the control group, in which no replacement reaction occurred. Thus, it appears that the contaminants were most likely removed from the solution through adsorption onto calcite, rather than by incorporation into the Ca-oxalate lattice during replacement. Thus, further experiments are needed to fully understand the conditions in which metals are affected by mineralogical changes.

2. Introduction

2.1 Groundwater pollution

Groundwater is commonly contaminated by various types of pollutants resulting from natural processes and human activity. These pollutants include household, municipal and industrial wastewater, landfills and toxic waste disposal sites, fertilizers and pesticides washed from agricultural land, radioactive waste, and heavy metals. The latter also commonly occur in natural conditions, where rocks contain poisonous heavy metals that may be washed into the groundwater. The pollutants seep into the groundwater reservoirs and may reach wells that provide drinking water (Shoval, 2006). Many heavy metals such as lead, mercury, arsenic, zinc, and cadmium, which are often found in contaminated soils and aquifers, are toxic to humans. Thus, developing and establishing a suite of methods for removing toxic heavy metals from drinking water is an environmental challenge of utmost importance in a world where access to clean water becomes increasingly limited following industrialization (Wongsasuluk, 2014).

2.2 Treatment of contaminated groundwater

There are two main approaches for treating contaminated groundwater. The first involves the removal of pollutants while pumping water out of the aquifer (ex-situ treatment). In case the pollutants are dangerous to the environment, they will be cleaned and treated, and the water will consequently be injected into the aquifer. The limitations of this method are the lengthy duration of this treatment and its high costs. The second approach relies on the introduction of compounds that can purify the aquifer without extracting the water (in-situ treatment). During this treatment, substances capable of adsorbing pollutants or neutralizing them to non-hazardous materials are injected into the aquifer. These materials treat the pollution within the aquifer, thereby eliminating the necessity to extract the groundwater.

Such long-term storage of pollutants in underground reservoirs has been proposed as a solution that has the best potential for sustainable treatment of pollutants, as they remain "imprisoned" within the rock (Soga, 2004). Nevertheless, these treatment methods are currently of limited ability to treat large areas and the deep depths. To improve the capability of these methods to treat large scale contamination,

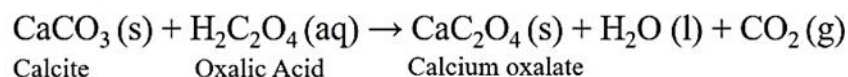
the treatment must not be limited to a specific location within the aquifer but instead should operate within aquifer increasing volume and continue to remove pollutants.

In this project, I will try to evaluate the effectiveness of a method for purifying groundwater contaminated with heavy metals that will meet these criteria, and will be cost-effective in both time and resources, and not limited to a specific locality.

2.3 Replacement reactions

When reactive solutions are introduced into the aquifer, the minerals that make up the aquifer's rocks come in contact with the solution and the system (mineral + solution) momentarily enters disequilibrium, and the chemical reaction "moves" towards equilibrium. When a mineral is completely out of its stability region, another mineral that is more stable under the new conditions may replace the original mineral. These mineral replacement reactions are very common and occur naturally in the environment (King, 2014).

One of the naturally occurring replacement reactions in natural water systems is the replacement of calcite by Ca-oxalate. Lichens, fungi, and bacteria emit oxalic acid that can replace calcite with Ca-oxalate (Ruiz-Agudo, 2013). The replacement product of this reaction (Ca-oxalate) is more stable and resilient and is less soluble than the calcium carbonate minerals, especially in an acidic environment (Matteini, 2008). These features have led to the development of a method for preserving ancient structures and sculptures built of carbonate rocks, in which solutions with oxalic acid are applied onto the surface of the stones in a controlled manner to obtain a durable layer of calcium oxalate through a mineral replacement process (Doherty, 2007). The reaction occurs spontaneously in standard conditions of room temperature and surface pressure, and the resulting Ca-oxalate minerals are safe for humans and the environment (Equation 1; Doherty, 2007; Matteini, 2008).



Equation 1- The replacement reaction of calcite into Ca-oxalate.

2.4 Oxalate and heavy metals

Heavy metals in the aquifer may precipitate as separate trace minerals or be incorporated into the primary mineral (Ca-oxalate) as secondary phases (Figure 1; McBride, 2017). However, the extent by which toxic heavy metals from groundwater are incorporated into the replaced mineral lattice is unclear, which limits the applicability of this method for groundwater purification.

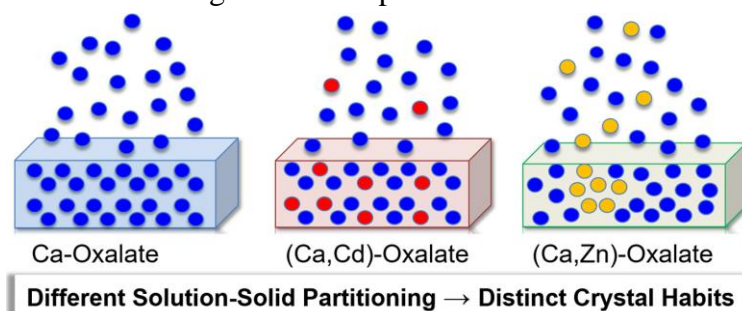


Figure 1 – Modes of heavy metals coprecipitation during Ca-oxalate precipitation. Left: pure Ca-oxalate. Middle: incorporation of contaminants into the Ca-oxalate crystal lattice. Right: the precipitation of a secondary Zinc-oxalate phase within the Ca-oxalate framework (McBride, 2017).

A variety of toxic metals, such as Pb, Zn, Cd, and Co may precipitate into the replacement product concurrently with the precipitation of calcium oxalate. Furthermore, calcium-oxalate is characterized by extremely low solubility (relative to calcite), especially under acidic conditions. At acidic conditions of $\text{pH} = 5$, for example, Ca-carbonate minerals are 20 times more soluble than calcium oxalate (Matteini, 2008). Therefore, if heavy metals are indeed incorporated into the Ca-oxalate lattice, they can be effectively locked in the replaced rocks for a long time and prevent environmental pollution. The use of this replacement reaction may contribute to the development of innovative methods for removing metals from aquifer dominated by carbonate rocks, such as the mountainous aquifer in Israel.

3. The research objective

The research aim is to answer to the following question: what is the extent of replacement reaction of calcite into Ca-oxalate toward removing heavy metals from groundwater in carbonate aquifers?

4. Research Methods

To evaluate the applicability of calcite replacement into Ca-oxalate in removing pollutants from carbonate dominated aquifers, I conducted a set of experiments in which the effectiveness of pollutant removal by calcite replacement into Ca-oxalate was evaluated through the mixing of oxalic acid and limestone in the presence of heavy metals. To determine the mode by which the pollutants in the solution were removed from the solution, the experiment included three subsets:

subset 1- replacement reaction experiments were carried out in Teflon bottles, where a solution that contains pollutants was placed along with oxalic acid and limestone fragments.

subset 2- experiments to determine separate precipitation of oxalate phases were carried out by mixing a solution of pollutants and oxalic acid in Teflon bottles without limestone.

subset 3- sorption experiments were carried out in plastic test tubes where a solution of pollutants was mixed with limestone but without oxalic acid.

Each of the experiment's subsets was conducted in six vessels, one for each type of the considered contaminants (table 1). The limestone used in the experiment is micritic limestone characterized by an average crystal size of ~5 micrometers, extracted from the Solnhofen Formation in Bavaria, Germany (table 1). The limestone was cut into equal square samples of 1.5 by 1.5 cm and a thickness of 1.5 to 3 millimeters. The rocks were weighed with an analytical scale and photographed on a millimetric paper for measurement of scale and size. In order to induce the replacement reaction of the mineral calcite, which is the dominant mineral of the studied limestone into calcium oxalate, I prepared 500 ml solution of 0.1 M of oxalic acid using double-distilled water (DDW, characterized by 18.2 megohm-cm resistance, distilled using a Thermo Scientific™ Barnstead™ GenPure™ Pro Water Purification System), and powdered oxalic acid dihydrate by Merck ($C_2H_2O_4 \cdot (H_2O)_2$). Also, a contaminant of known concentration was placed in each experiment bottle. Several pollutants were used in 200 ppb concentration (table 1), in each of the experiment's subsets to determine whether their concentration changed due to its contact with calcite, oxalic acid, or both. The bottles were set with a contaminant concentration of 200 ppb in 50 ml solution of

distilled water or oxalic acid with or without limestone, and placed on a rocking bench, to prevent solution differentiation within the vessel.

The vessel was sampled 6 times after 0.5, 1, 2, 4, 8, and 24 hours. In each sampling, 0.5 ml of each bottle was sampled using a pipette and consequently mixed with weak 1.5 ml HNO₃ in a 5 ml vial to prepare them for measurements using an ICP-MS. The vials were labeled by the experiment's subset from 1-6 (according to the sampling time). For example, a sample taken during the third sampling from bottle F was registered as F3. Between each sampling, the tip was washed with distilled water and replaced after six samples. After the last sampling, the solution was removed, and the rock samples were dried in the oven at 60°C and analyzed using X-ray diffraction. During the wash of rock samples M and J, I noticed that the samples were abnormally dissolved and a large number of precipitates were present at the bottom of the vials. These samples disintegrated and fell into the water during the rinsing of the samples.

Bottle Label	Subset	Contaminant type	Sample weight
A	Group 1	Pb standard (Merck)	1.74
B	Group 2	Pb standard (Merck)	None
C	Group 3	Pb standard (Merck)	0.877
D	Group 1	As standard (Merck)	1.422
E	Group 2	As standard (Merck)	none
F	Group 3	As standard (Merck)	1.450
G	Group 1	Zn standard (Merck)	1.851
H	Group 2	Zn standard (Merck)	none
I	Group 3	Zn standard (Merck)	1.38
J	Group 1	Cs standard (Merck)	1.353
K	Group 2	Cs standard (Merck)	none
L	Group 3	Cs standard (Merck)	1.467
M	Group 1	Optima 3000 Perkin Elmer*	1.3

N	Group 2	Optima 3000 Perkin Elmer	none
O	Group 3	Optima 3000 Perkin Elmer	1.74
P	Group 1	Merck IV**	1.293
Q	Group 2	Merck IV	none
R	Group 3	Merck IV	1.175

* Optima 3000 - Contaminant solution. Details in Appendix 2.

** IV - Contaminant solution. Details of the pollutants in Appendix 3.

Elemental concentrations were determined using ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). This device samples the solutions and stimulates the ions using plasma. The ions are consequently accelerated into a vacuum chamber that allows accurate measurement of the elemental concentration in the solution by separation under a magnetic field according to the charge to mass ratio of each species.

To characterize the solid phases before and after the experiment, XRD (X-ray Diffraction) was used. This method determines the crystalline structure of the substance through the comparison of measured X-ray diffraction patterns with a previously-determined mineral catalog.

5. Results

5.1 XRD (X ray diffractograms)

To test for the replacement of solid phases, XRD measurements were used to identify the mineralogical phases. The mineral phase analysis was carried out before the experiment and for the group that was mixed with oxalic acid (Group 1) since only in that subset the basic conditions for calcite replacement reaction existed (Figure 2). According to the XRD, the replacement group can be divided into two subgroups. Subgroup 1 includes subsets A, D, and G, in which different concentrations of Ca-oxalate were observed, and thus it is evident that the replacement reaction took place. In these bottles most of the oxalate phases observed were monohydrate, but dehydrated phases were also detected. In subgroup 2, which includes subsets J, M, and P, where no Ca-oxalate was observed, which testifies that no replacement reactions took place. These results agree with the visual inspection of the limestone during the experiment. In these bottles, the oxalic acid seemed to have a more serious effect on the calcite, and

the solution in these bottles was filled with white-gray substance and the sample was covered with a murky white layer. In the meanwhile, the M and J samples fell during the wash to the wash water and the observed white particles may have been washed and thus not left for the XRD analysis. It is possible that for example P, important particles were washed and did not remain until the XRD analysis.

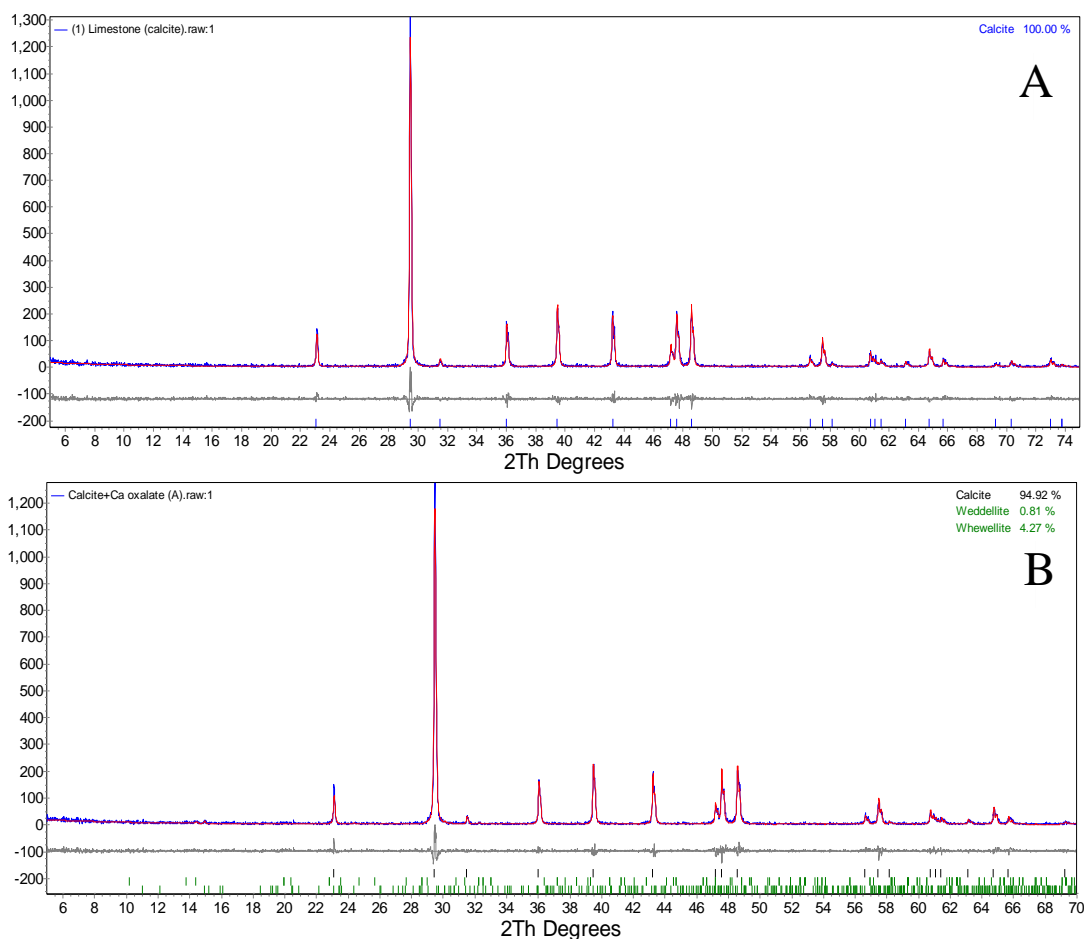


Figure 2- X-ray diffractograms of (a) Solnhofen limestone, where the rock is made up of 100% of the calcite mineral (detailed composition from top right). (b) Solnhofen limestone after the reaction with oxalate, where calcium oxalate monohydrate and calcium oxalate dehydrate formed (detailed composition from top right).

5.2 Elemental determination using ICP-MS

Raw concentration measurements were processed into graphs showing the change in pollutant concentration as time-dependent. I divided the results of the different pollutants into three groups showing distinct patterns. 1. Pollutants that demonstrated a decrease in the pollutant's concentration only in the replacement group. 2. Pollutants that demonstrated a decrease in the pollutant's concentration in the replacement group and the adsorption group. 3. Pollutants that showed no decrease in pollutant concentrations or only a slight decrease.

5.2.1 Pollutants that were removed by chemical replacement

Figure 3 summarizes the results of the experiments in which there was a decrease in the concentration of pollutants only in the experiments of the replacement group. A significant decrease was measured in the concentration of nickel, that reduced from 176 to 32 ppb after 24 hours, whereas no significant change was observed in nickel concentrations in the other groups (Fig. 3a). An additional decrease was observed in the replacement group for barium, where concentrations reduced from 22 to 12 ppb (Fig. 3b). In contrast, barium concentration increased slightly in the other groups.

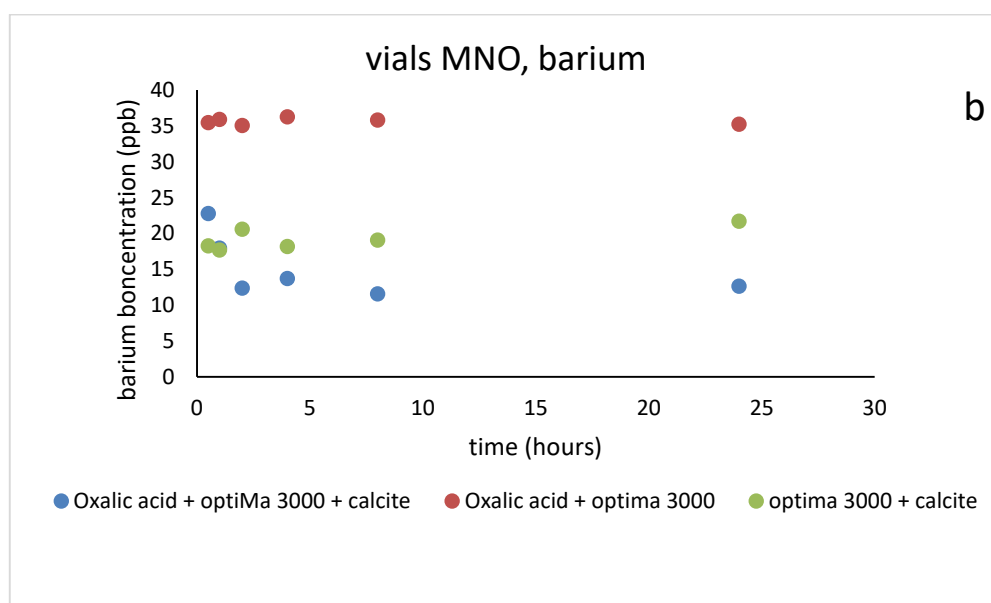
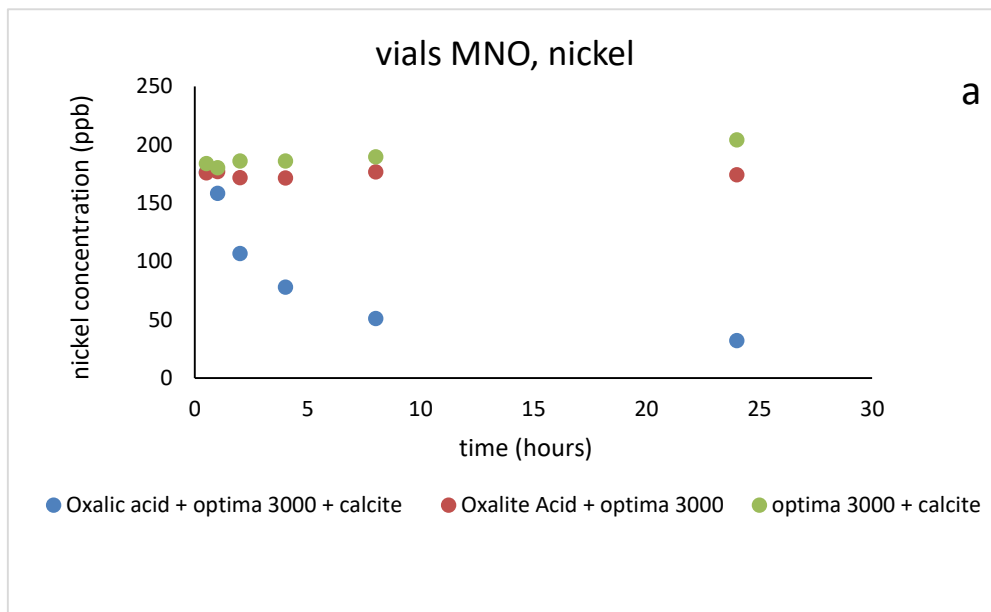
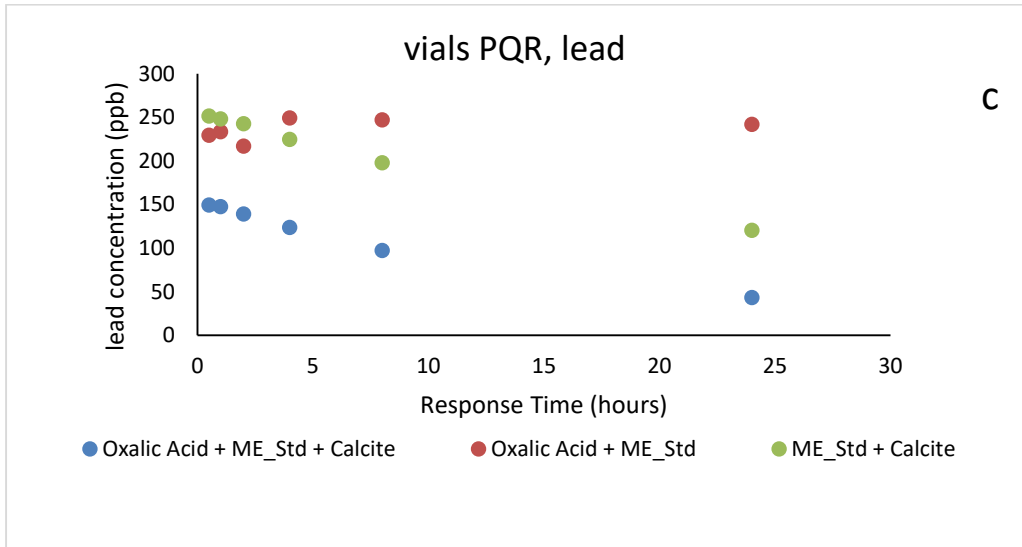
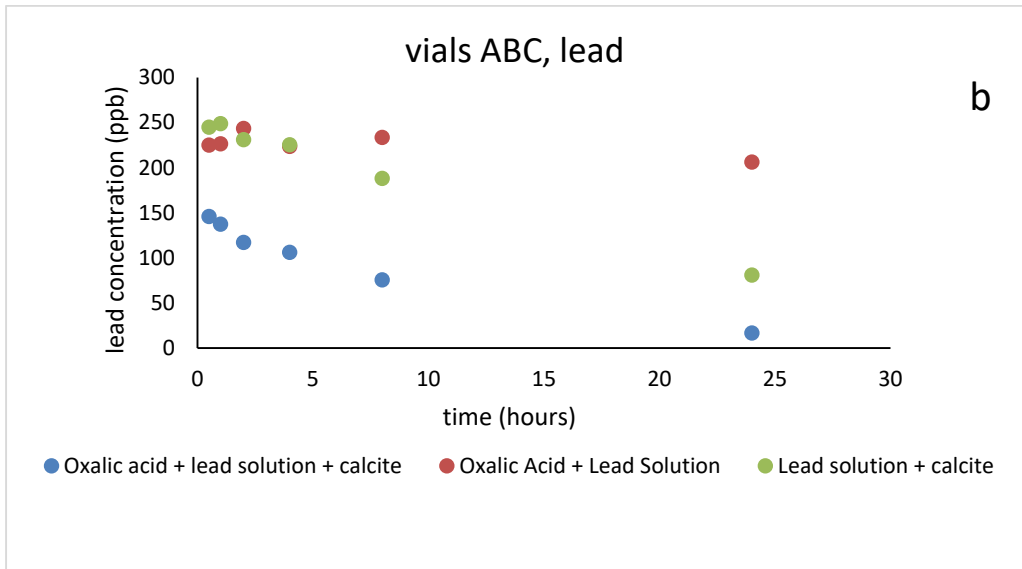
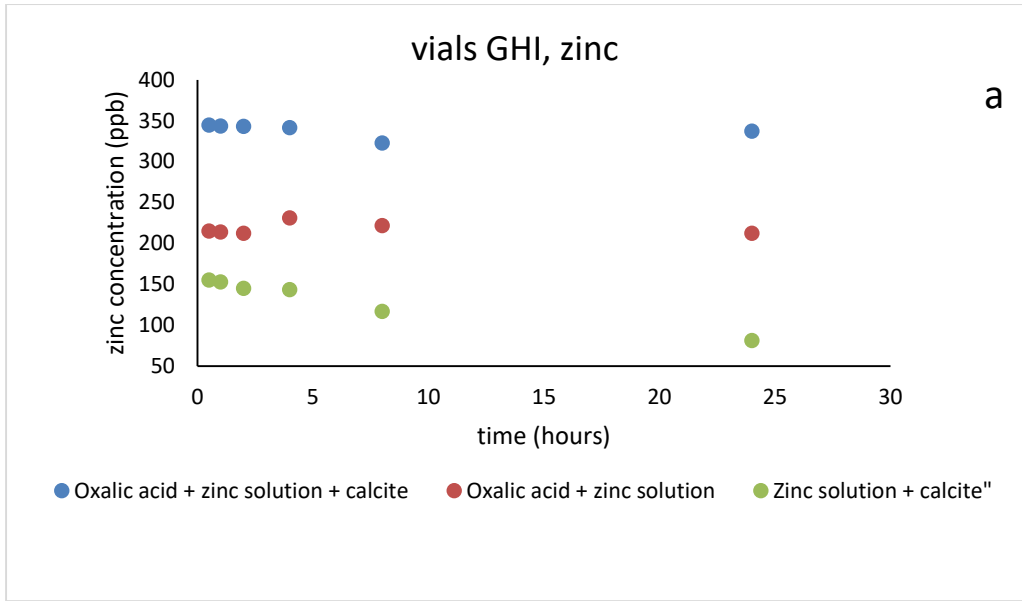


Figure 3 Pollutants that showed a decrease in pollutant concentrations only in the replacement group. Nickel (a) and barium (b) concentrations during 24 hours of monitoring. Azure - a bottle containing calcite, pollutant, and oxalic acid (replacement took place). Red - a bottle containing a pollutant and oxalic acid (no replacement took place). Green - a bottle containing calcite and pollutant (no replacement). Barium and nickel concentrations decreased in experiments in which replacement took place, but remained constant in experiments with no replacement.

5.2.2 Pollutants that were removed by chemical replacement and adsorption

Figure 4 summarizes the results of the experiments in which concentrations of pollutants decreased both in the replacement and adsorption groups. Zinc concentrations show a slight (and likely insignificant) decrease when no other pollutants were present in the substitution group- 344 to 337 ppb (Fig. 4a). In contrast, in the adsorption group, there was a more significant decrease in zinc concentration, where its concentration reduced from 155 to 81 ppb. Additionally, a significant decrease in lead concentration in both the replacement and adsorption groups was observed, where concentrations decreased from 146 to 16 ppb, and from 244 to 80 ppb, respectively. Figure 4c shows a significant decrease in lead concentration when in the presence of additional pollutants (as part of the Merck IV solution, appendix 2) in both the replacement and adsorption groups, where concentrations fell from 149 to 43 PPB, and from 251 to 120 PPB, respectively. In contrast, little increase in lead concentration was marked in the precipitation group. Figure 4d shows a decrease in cadmium in the presence of additional pollutants (IV) in the replacement group and the adsorption group, from 154 to 95, and from 244 to 158 ppb, respectively. In contrast, the cadmium concentration in the precipitation group increased from 227 to 239 ppb.



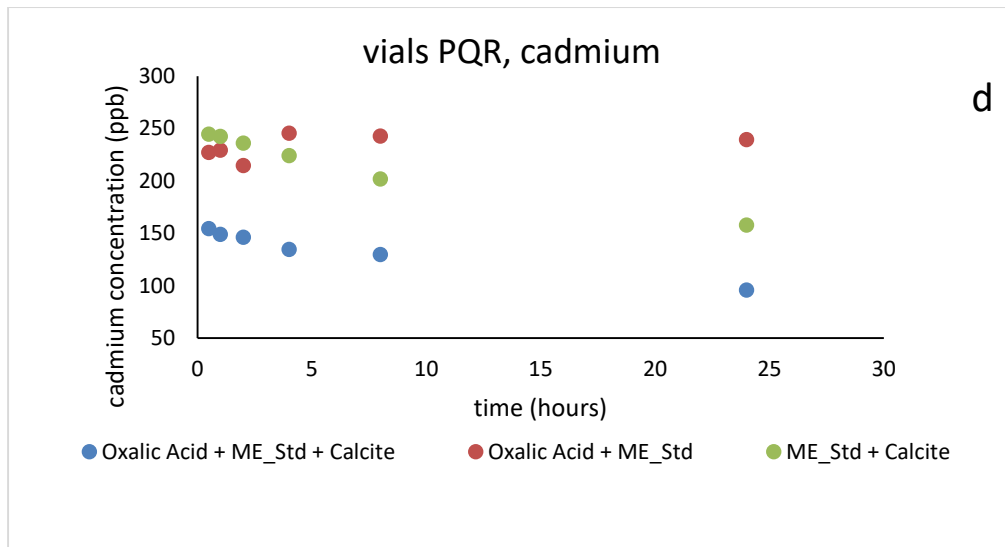
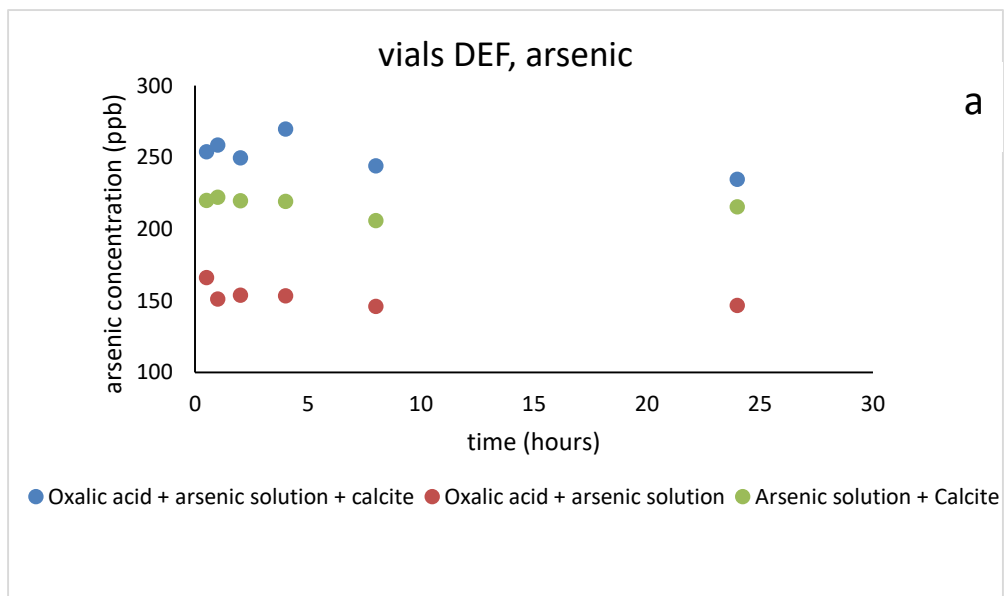


Figure 4 Pollutants that show a decrease in concentrations in both replacement and the adsorption groups. Concentrations of zinc (A) lead (B - C) and cadmium (D) vs. time. Azure - bottles containing calcite, pollutant, and oxalic acid. Red - bottles containing pollutants and oxalic acid. Green - bottles containing calcite and pollutant. The concentration of zinc, lead, and cadmium decreased in experiments in which replacement or adsorption took place and did not change in the precipitation experiments.

5.2.3 Pollutants that showed no change in concentrations by chemical replacement and adsorption or direct precipitation

Figure 5 summarizes the results of experiments where no significant changes occurred in any of the subsets, and the contaminant concentrations remained constant throughout the experiment. Figure 5a shows a slight decrease in the three groups, of about 10-20 PPB. This decrease is not significant with respect to the high concentrations used in the experiment.



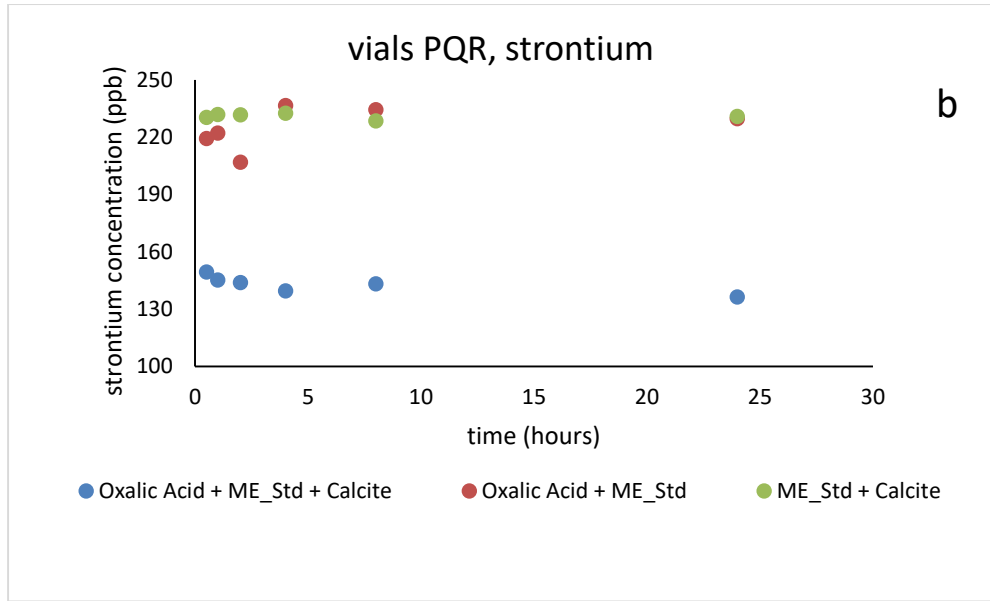


Fig. 5 Experiments that showed no decrease in the pollutant concentration. Azure - bottles containing calcite, pollutant, and oxalic acid. Red - bottles containing a pollutant and oxalic acid. Green - vials containing calcite and pollutant.

6. Discussion

6.1 The effects of calcite replacement reactions to Ca-oxalate in the presence of contaminants in aquifer rock

The results of the XRD analyses show that in some of the experiments, the replacement reaction of calcite into Ca-oxalate has taken place. However, at first glance, the results may raise some concern, as half of the bottles in the calcite replacement group were not replaced at all with Ca-oxalate. This result is even more puzzling, as these samples also show a decrease in the number of pollutants in the replacement group. For example, Fig. 3a, which describes the concentration of nickel in vial M, shows that on one hand, no replacement of calcite into oxalate has taken place (as evidenced by XRD), but a significant decrease in the concentration of nickel in the replacement group, which requires replacement, was observed. One possible explanation for this contradiction is that the oxalate phases in these samples were precipitated alongside the calcite and were washed during rinsing. Indeed, in the limestone replacement experiment (Fig. 2B), 94.9% calcite, 4.27% calcium oxide monohydrate (Whewellite), and 0.8% calcium oxide dehydrate (Weddellite) were identified. Furthermore, there is no evidence of oxalate phases with heavy metals other than calcium oxalate, which indicates that the metals were incorporated into the Ca-oxalate lattice rather than precipitating as separate oxalate phases. Another possibility is that additional oxalate phases were precipitated but at a very low concentration so

that their detection via XRD was not possible. Future experiments in which the initial pollutant concentration is higher may help to understand whether pollutants have entered the Ca-oxalate precipitate or have precipitated as separate phases.

6.2 The effect of replacement reactions on the concentration of pollutants in the aquifer water

In the results chapter, I divided all ICP-MS results into three groups that showed distinct behavior. Several explanations could account for the different response documented in each of the groups, and whether some formulation that accounts for this distinctive behavior can be derived.

Two explanations can be sought in this regard: (1) the metals that responded to the replacement reaction are all metals whose size is similar or smaller than the calcium atom, so they successfully replaced the calcium within the oxalate mineral lattice, and (2) the metals that have undergone replacement are all divalent (with a double electric charge of +2) like calcium. It can be concluded that the replacement reaction is effective for metal fixation in the carbonate aquifer, only when the metals ions fulfill the abovementioned conditions.

All the ICP-MS results raise the question of why the initial concentrations are not equal, even though the quantities of pollutants I put into each of the bottles were calculated to ensure that the concentrations are equal. Two explanations can be provided regarding this question: 1) sampling for the first measurement was carried out about half an hour after the beginning of the experiments and it may be that by this time the concentrations had already changed significantly. This is supported by Fig. 3a, where most of the changes in concentration had occurred during the first four hours, so the most significant decrease is expected to take place at the beginning of the experiment. 2) We may have made an error in the calculation or preparation of the initial pollutants introduced into the solutions because the volumetric measurement error of the pipette that I used was significant concerning the quantities.

I propose two ways to deal with the two problems I raised about the experiment, respectively: 1) the pollutants' concentrations should be sampled and measured at time 0, immediately after the experiment was set, and 2) prepare the contaminants solution together for each vials trio, and then split them into the experiments vials.

In conclusion, the results of this study demonstrate that for some metals, such as nickel and barium, the replacement of calcite into Ca-oxalate is indeed effective in cleaning groundwater. For other metals, including lead, cadmium, and zinc, replacement reaction showed a decrease in the pollutants' concentrations, but a similar decrease occurred in the adsorption experiments and it is therefore difficult to determine from these experiments what causes their decrease in concentrations. Other metals showed no significant change in concentration and therefore this procedure may be considered ineffective for their purification. Repeating these experiments and conducting additional experiments under additional conditions, focusing on the barium, nickel, zinc, lead, and cadmium can help answer the questions that remained open.

7. Conclusions

In this work, I evaluated the effect of calcite replacement into Ca-oxalate reaction on heavy metal concentrations in water. It was found that oxalic acid in the presence of limestone results in the desired replacement reaction and a decrease in pollutant concentrations was also validated by ICPMS for some metals due to the replacement reaction. Although the concentrations of some of the metals have also declined in the control group, the results indicate that utilization of the calcite to Ca-oxalate replacement reaction shows a promising possibility for the removal of heavy metals from groundwater in carbonate dominated aquifers. Naturally, the preliminary nature of this work leaves many open questions that require further investigation. These include the determination of the conditions under which metals are most positively affected by the mineralogical replacement reaction, what are the limitations of this method, and what are the implications of applying it in large scales. Further controlled conditions experiments could help answer at least some of these questions in the future. I believe that this research is expected to contribute to future research by focusing future investigations on metals that showed promising results. Such experiments can help determine the conditions under which this method can be utilized effectively to reduce the concentrations and perhaps even eliminate the presence of toxic heavy metals in groundwater while locking the contaminants in newly precipitated oxalate phases.

8. References

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9. Appendices

1. List of pollutants multielement standard optima 3000 (Perkin Elmer):

1ppm	Ba (Barium), Mg (Magnesium)
10ppm	La (Lanthanum), Mn (Manganese), Ni (Nickel), Zn (Zinc)
50ppm	As (Arsenic), K (Potassium)
2%	HNO ₃

2. List of pollutants ICP multi-element standard solution IV (Merck):

Ag (Silver)	1000 mg/l	K (potassium)	1000 mg/l
Al (Aluminum)	1000 mg/l	Li (Lithium)	1000 mg/l
B (boron)	1000 mg/l	Mg (Magnesium)	1000 mg/l
Ba (barium)	1000 mg/l	Mn (Manganese)	1000 mg/l
Bi (bismuth)	1000 mg/l	Na (sodium)	1000 mg/l
Ca (calcium)	1000 mg/l	Ni (Nickel)	1000 mg/l
Cd (cadmium)	1000 mg/l	Pb (lead)	1000 mg/l
Co (cobalt)	1000 mg/l	Sr (Strontium)	1000 mg/l
Cr (chromium)	1000 mg/l	Tl (Thallium)	1000 mg/l
Cu (Copper)	1000 mg/l	Zn (Zinc)	1000 mg/l
Fe (iron)	1000 mg/l		
Ga (Gallium)	1000 mg/l		
In (Indium)	1000 mg/l		