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Prevention of Scaling by Quick Removal of Metals from the Brine via Adsorption

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ABSTRACT

Scaling (= mineral precipitation) in geothermal plants occurs due to oversaturation of salts caused by changes in the chemical equilibria during processing of thermal water. Since salts are composed of a cationic and an anionic part, uncontrolled precipitation can be avoided if the cation (often a heavy metal) is removed from solution by a sorption technique to concentrations below mineral saturation. Various sorption techniques are known from groundwater purification, but have never been applied in geothermal plants. For industrial use in such environments the adsorption material needs to be of low costs, temperature resistance, large sorption capacity at quick removal, and ideally it can be reused after cleaning/ regeneration.

In this study three different sorption materials were tested to eventually develop a filter material that removes scaling-inducing elements below their saturation: Zeolite (highly porous alumosilicates), chitosan (a biopolymer obtained by deacetylation of chitin), and magnetite (Fe_3O_4; a magnetic mineral with high surface area). While zeolites and iron oxides could be added as seed material to the thermal water in a first step and be removed by particle filtration in a second step, the chitosan can be processed into fiber mats and integrated in a filter system directly. Mineral saturation was calculated for various conditions by PhreeqC to ensure that the metal removal process was not by mineral precipitation. The three sorption materials were tested at various salinities (0-2 M NaCl) in a batch attempt. In addition, a flow-through reactor was developed to investigate the ability of these materials for removing the scaling-relevant metals lead, barium, copper, and iron from geothermal brine under near-geothermal, flowing conditions.

1. INTRODUCTION

A key operational challenge in geothermal energy production is restricted flow. During power plant operation, both the geothermal fluid and the reservoir are constantly prone to chemical and physical changes that can seriously affect the efficiency of the fluid flow cycle – from production to injection. Productivity and injectivity often substantially deteriorate over time, despite initially successful well testing. A major obstacle for providing sufficient geothermal flow is scaling (mineral deposition) inside the installations, wellbore, and the reservoir. Scaling occurs in all types of geothermal fluids. However, in particular fluids from highly saline, sedimentary geothermal reservoirs are poorly understood and scaling can hardly be predicted based on common equilibrium calculations due to incomplete databases for high salinity and high temperature conditions. Scaling prevention methods are so far typically related to the addition of chemicals to the brine which complex the scaling-responsible metals and keep them as aqueous complexes in solution. However, those inhibitors often are expensive and of uncertain long-term risks to the reservoir as the stability, biological degradation and persistence of those complexes is largely unknown. The EU Horizon2020 GEOTHERMICA project PERFORM "Improving Geothermal System Performance through Collective Knowledge Building and Technology Development" investigates methods to prevent scaling by decreasing the metal concentration in the brine to a level below the mineral saturation at a given temperature and thus prevent scaling. The challenge is to quickly remove the metals by using metal binding materials either directly as a filter material or as additive in a separate container to have it reacted with the geothermal fluid and afterwards filter it off together with the bound metals. The process of ions (=adsorbates) removal by binding them to the surface of a solid phase is called adsorption. The adsorbing materials (adsorbent) need to be stable at the given high temperatures and salinities in geothermal systems.

This study aims at testing different potential adsorbents for the application at geothermal conditions. Especially the effect of salinity and temperature on the adsorption will be investigated. Due to the high relevance of the frequently occurring scaling minerals barite ($BaSO_4$), lead- (e.g. as laurionite PbOHCl), or copper (Cu) phases (e.g. at the Groß Schönebeck geothermal site; Regenspurg et al., 2015), this study investigates the removal of the responsible cations Ba^{2+}, Pb^{2+}, and Cu^{2+} (as adsorbates) from the brine. The adsorption process of three different materials with very different material properties was investigated. These materials are:

- Zeolites, are a group of aluminosilicate minerals with microporous structure and variable composition given by the general formula $[(Li, Na, K)_a(Mg, Ca, Sr, Ba)_d(Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}]\cdot mH_2O$ (Moshoeshoe et al., 2017). The high adsorption capacity is due to a high surface area together with an additional inner surface (inner pores) that allows to incorporate metals also within these pores. Therefore they are frequently used as commercial adsorbents and catalysts for example for waste- and drinking water purification systems or nuclear-waste reprocessing because of their micro-porous ability to capture some ions while allowing others to pass freely. This allows many fission products to be efficiently removed from the waste and permanently trapped. Due to its net negative charge and exchangeable cations they are suitable especially for removing heavy metal cations (Erdem et al., 2004). Zeolites are frequently occurring natural minerals with high thermal stability but there is also a large range of artificially synthesized zeolite minerals with different structures and very well defined properties.

- Magnetite is one of the most frequently occurring iron oxide minerals (Fe_3O_4) but can also be easily produced artificially (Cornell & Schwertmann, 1996). It has ferromagnetic properties and due to its large surface area (10-100 m^2/g; Cornell & Schwertmann, 1996) the ability to bind large amounts of both, cations (at neutral to basic pH-values) and anions (at acid pH-values) to its surface (adsorption). Its application for water purification was investigated for example for Cr(VI) by Lasheen et al. (2014).
- Chitosan is less investigated for its application in water purification as compared to the other two materials, although its properties are very promising. It is industrially used for the purification of food and pharmaceutical products. Chitosan is a bio-based sorbent obtained by deacetylation of chitin (poly(β-(1→4)-N-acetyl-D-glucosamine), which can be derived from shells of crabs and shrimp and which is the second-most abundant biopolymer in the world. Studies have shown a large adsorbing capacity for cations, especially heavy metal adsorption (Celik et al., 2017; Bailey et al., 1999). By generating fibre mats from electrospun chitosan, this material can be fashioned with extremely large surface areas and thus used as adsorptive filter material suitable for geothermal application (Celik et al., 2017).

To find out, which of these materials can be best used to filter out certain metals of the geothermal fluid in dependence of variable geothermal conditions, a set of different experiments was developed that are scaled up from simple, static batch to near-geothermal flowing conditions, which is however much too long to be applicable for geothermal purposes. One experimental setup was running between one and 120 minutes to determine the amount of metal that can be removed from a brine in a short time. This is very relevant when using the material as a filter or as an additive within a reaction container. For comparison, other experiments were run for up to two weeks to obtain equilibrium conditions. For simulating geothermal conditions, experiments will be also conducted at elevated temperatures and at various conditions in a flow-through reactor. Eventually, results of this study should give kinetic parameter of metal adsorption that can be implemented into geochemical models to be used for power plant optimization. Within this paper, initial results from the static batch experiments are shown.

2. MATERIALS AND ANALYSIS

The three materials used for metal removal (zeolite, magnetite, chitosan) were characterized before the experiments by various methods:

The white zeolite powder from a natural source was characterized by X-ray diffraction to consist of predominantly clinoptilolite ($(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$) with traces of quartz, heulandite (another mineral of the zeolite group forming solid solutions with clinoptilolite), and biotite. Two different types of clinoptilolite-zeolite (both of different origin with slightly different mineralogical composition) were tested for adsorption (referred here as zeolite I and zeolite II). If not indicated otherwise, however, zeolite I was used in the experiments.

Magnetite (Fe_3O_4) was first directly precipitated onto pure quartz sand grains to allow a better handling of the material. This was necessary because pure magnetite nanoparticles can very easily be transported in solution and pass through most filters of a geothermal power plant.

The chitosan was obtained from the TU Dresden (degree of deacetylation DD = 95%, viscosity mean molar mass M_v = 200 kDa). As an organic biomaterial it is prone to thermal degradation at elevated temperatures. To increase temperature stability this material will be chemically modified. However, within the present study, first experiments were performed with the raw material as flakes. The flakes were conditioned by washing with ultra-pure water, drying at 50 °C, and storing in a desiccator under vacuum.

For all three adsorbents, the surface area was determined by the BET method. For zeolite and magnetite nitrogen (N_2) and for chitosan helium (He) was used as adsorbing agent.

Elemental Analysis for Pb, Ba, and Cu was performed by inductive-coupled plasma mass spectrometry (ICP-MS) according to DIN EN ISO 17294-2(E29):2017-01. The detection limit for Cu, Ba and Pb is below 0.001 mg/L.

Equilibrium calculations: Saturation indices were calculated by PhreeqC using the *Thermodyn* database for various temperatures (25-150 °C) and NaCl contents (0.1, 1, 2 M) for solutions with 1 mM of either Pb, Cu, Fe, Ba or all of them.

3. METHOD DEVELOPMENT

The approach within this study is to test first the three adsorbent materials alone or altogether at various salinities in a static batch experiment at room temperature. The extent of adsorption was analysed at different time intervals as well as after two weeks at the static equilibrium. The most promising combinations will be used for tests at higher temperature and scaled-up in a up flow-through apparatus. This instrument allows to test them either for an application as filter material or as absorbent additive that will first react with the metal ions and afterwards will be filtered out.

3.1 Static batch experiments

Experiment I: The mass of the adsorbent (two types of zeolite: zeolite I and zeolite II) was varied (0.01, 0.075, and 0.15 g/L) and the experimental solution (Ba concentration of 5.8 mg/L and NaCl concentration of 10 mmol/L) was brought to equilibrium by continuously shaking over two weeks. In the beginning of the experiment the pH-value of each solution was adjusted to 6 ± 0.1. At the experiment end, the remaining Ba concentration in the solutions was measured by ICP-MS.

Experiment II: Both types of zeolite were used in 3 different solid - solution ratios (5, 25, and 50 g/L). All three metal salts (Cu, Ba, Pb) were added (5.2 mg/L, 7.9 mg/L, and 2.2 mg/L, respectively) and subsamples taken and analysed at various time steps (between 5 minutes and two weeks).

Experiment III: Each 14 mg of the solid material (scale accuracy 0.1 mg) was added into a septum glass bottle and 35 ml of electrolyte solution with metal (0.1 M, 1 M, or 2 M NaCl with 1 mM $BaCl_2$, $PbCl_2$, or $CuCl_2$) was added (0.4 g/L adsorbent) and continuously stirred. For each adsorbate/adsorbent ratio, eight replicates plus a blank were prepared. Immediately after metal addition, the suspensions were stirred and the experiment stopped after 1, 2, 4, 8, 16, 32, 64, and 128 minutes. The pH-value was measured in a subsample before and after each experiment. After each reaction time step, the suspension was filtered (0.45 µm) and acidified (with HNO_3 to pH <2) to measure the metal content.

3.2 Up-scaled kinetic experiments at elevated pressures, temperatures and flowing conditions

For experiments at elevated temperatures and pressures a flow-through reactor has been developed that allows to test the adsorbent materials at non-static conditions and to measure in-situ the changes in the fluid chemistry. The set up can be changed depending if the adsorption material is tested directly as a “cation filter” or as an additive that will be filtered out afterwards.

3.2.1 Technical description of the flow-through reactor

The flow-through fluid monitoring and reaction system (FluMoRe) permits comprehensive process investigation at pressures up to 40 bar and temperatures up to 200 °C. Central to the device are two reactor vessels made of duplex steel 1.4462 that can hold up to 50 L of fluid each and sensors can be introduced through the top or bottom lid (Fig. 1). The reactors can be operated individually (fluid monitoring) and both reactors can be stirred (magnetically coupled stirrers DTS) and actively heated with mantle heaters up to 160°C. Most components and add-ons are made out of corrosion-resistant materials such as titanium or Hastelloy. The other remaining pipes as well as the filter housing are made of stainless steel.

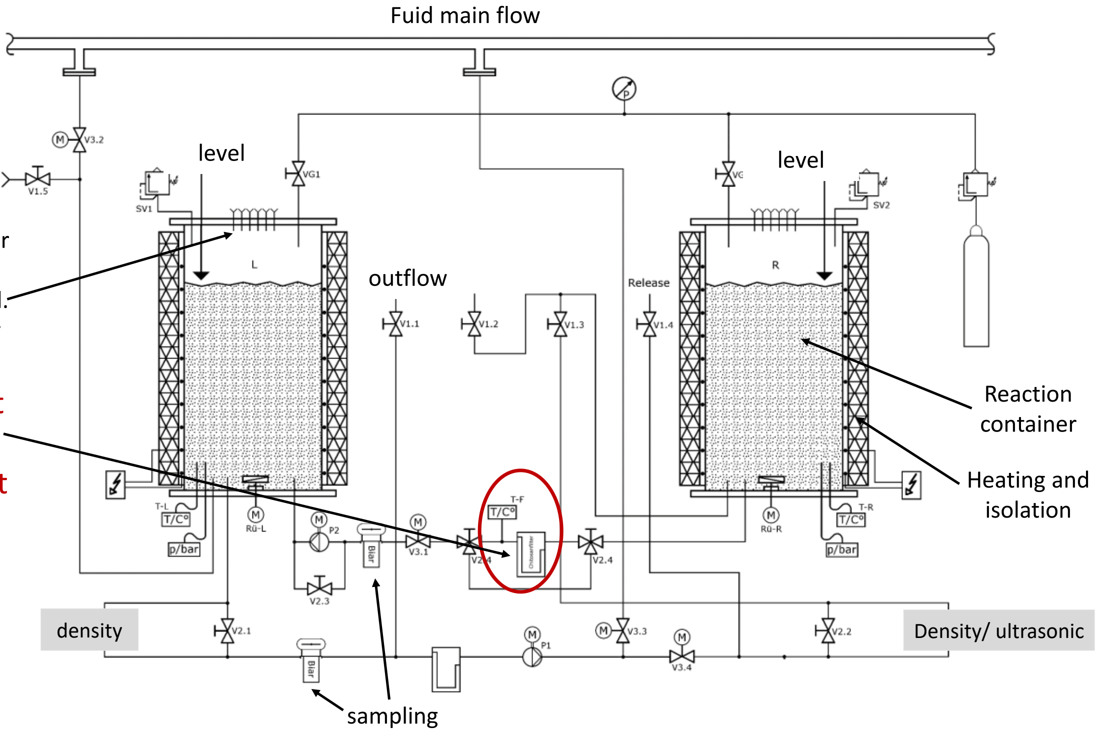

Figure 1: Simplified technical drawing of the fluid monitoring reactor (FluMoRe) as developed by GFZ.

Permanent installations comprise one high temperature density meter as well as one combined density-sonic velocity meter and two sets of high temperature pH, redox, and conductivity probes. For each reactor one fluid sampler (BIAR) is provided that allows sampling at high experimental temperatures and pressures. Add-ons are, for each reactor, one sonic velocity and one corrosion monitoring probe. Also, fibre-optic sensor evaluation with a complete spectrometric system and turbidity measurements (VIS-NIR) can be conducted. Two gear pumps allow fluid circulation and two high precision syringe pumps permit fluid injection to provoke, for example, precipitation of solid particles in connection with defined investigations on scaling processes (Milsch et al., 2015).

3.2.2 Experimental Set up

The system was extended by integrating a filter housing connected between the two reactor vessels. This stainless steel flow-through filter unit can be loaded with 25 cm^3 of adsorbent material. The housing allows to perform experiments at conditions up to 350 bar and 200 °C although the conditions in the actual flow-through reactor are limited to 160 °C and 20 bar. The filter unit is equipped with a temperature sensor so that the temperature within the unit can be monitored online.

Within the dynamic experiments the metal ion (Ba^{2+}, Cu^{2+}, Pb^{2+}) containing fluid will flow through the filter unit (containing the absorbent) under high-pressure/high temperature conditions. The time available for the adsorption process can be controlled by the flow, which can be varied between 80 and 400 ml/min. The physico-chemical parameters of the fluid can be monitored before and after the filter unit. After the reaction the adsorbent can easily be removed from the filter unit and be analysed, exchanged, or reactivated if possible. These dynamic experiments can later-on be up-scaled for application of the adsorbent materials in a real geothermal filter at a test site of a geothermal plant.

Alternatively, static reactor experiments can be performed. Here, a certain amount of adsorbent (zeolite, magnetite, or chitosan) will be added to the given fluid of certain composition in one of the reactor vessels at certain high pressure/high temperature conditions. After injecting the metal to be removed (Pb^{2+}, Cu^{2+}, Ba^{2+}), the vessel will be stirred and the reaction is allowed to take place for a certain amount of time before the fluid will be pumped through the filter unit (containing a regular filter) to remove the solid particles and analyze the aqueous phase. In-situ measurements of pH, redox or electric conductivity in the reactor can be used to monitor the progress of adsorption. This can be of relevance, for example, for anion adsorption on iron hydroxide from the surface of the adsorbent, which results in the release of hydroxide ions and thus in a pH-increase. In addition samples can be collected from the reactor at high pressures and temperatures and be analyzed for the adsorbate concentration.

4. INITIAL RESULTS AND INTERPRETATION

Calculation of mineral saturation in test solutions

Mineral saturation at equilibrium was calculated for the given conditions (Cu, Ba, or Pb solutions at 0.1 M, 1 M, or, 2M NaCl) using the geochemical code PhreeqC (Parkhurst & Appelo, 1999). Results indicated that the mineral laurionite (PbOHCl) would be oversaturated for Pb solutions (1 mmol/L) at room temperature in 2 M NaCl (Fig. 2). Indeed, white precipitates were formed in solutions prepared at these conditions. This was previously confirmed in experiments with Pb^{2+} dissolved in sodium chloride solutions of various concentrations, where the formed precipitates were identified by XRD as laurionite (Regenspurg et al., 2016). Laurionite was also observed as scale forming mineral at the geothermal site in Groß Schönebeck (e.g. Regenspurg et al., 2015). Although the model also indicated slight laurionite saturation in 1 M NaCl solution, no precipitations were observed in test solutions. Consequently, adsorption experiments with Pb were performed only for 0.1 and 1 M NaCl, which remained undersaturated at ambient conditions. Similarly, in Cu solutions the mineral cuprite (Cu_2O) was calculated to be oversaturated. In contrast to the experiment with Pb, no precipitates were observed in Cu solutions indicating that the formation is kinetically impeded.

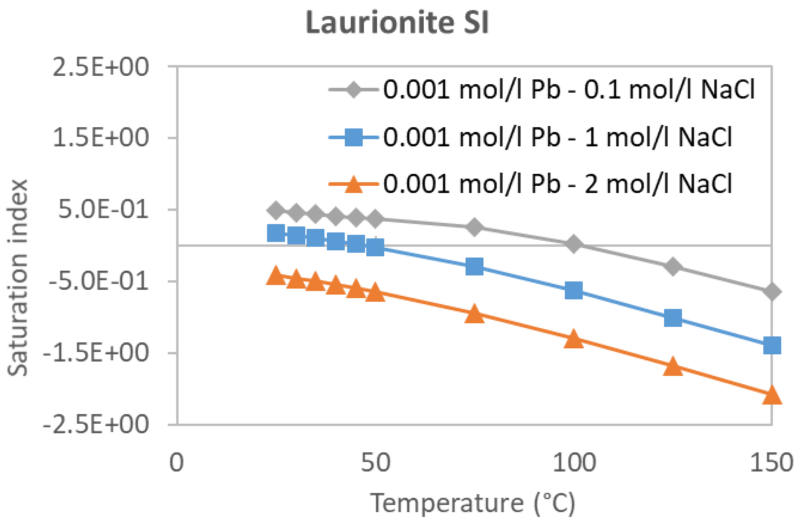

Figure 2: PhreeqC calculated saturation index for laurionite (PbOHCl) in dependence of salinity and temperature.

Static batch experiments at room temperature

Experiment I: The effect of varying the amount of adsorbent (zeolite I and II) at constant metal (Ba) concentration was studied in a first attempt: 0.01, 0.075, and 0.15 g /L zeolite were added to a 5.8 mg/L Ba solution. After equilibrium (2 weeks reaction time), the remaining Ba was measured and from this value the adsorbed Ba concentration calculated by the difference to the initial Ba concentration. The data showed that between 30 and 75 mg/g Ba can be taken up by zeolite (Fig. 3). Zeolite I performed slightly better as compared to zeolite II. The adsorption capacity and the effect of total Ba sorption (mg/g) was in the same order of magnitude when comparing with a short term-experiment (zeolite I after 2 h; Fig. 3), where about 45 mg/g Ba were adsorbed (1mM initial Ba concentration).

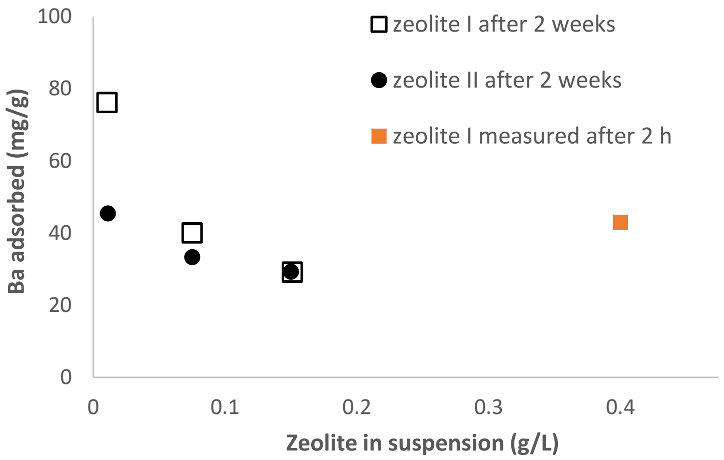

Figure 3: Ba adsorption per mass adsorbent (zeolite I and II) in dependence on the mass of adsorbent after 2 weeks and after 2 h.

Experiment II: Results obtained after adding all three metal containing solutions simultaneously into zeolite suspensions (both, type I and type II) with various solid:solution ratios (5, 25, 50 g/L) are presented in figure 4. Especially Ba and Pb ions were removed relatively quickly, whereas Cu removal was clearly lower and slower. Again, zeolite I (white and grey colors) performed slightly better as compared to zeolite II (blue colors in figure 4). At the given relatively low concentration of adsorbate nearly 100 % of Cu and Pb adsorption was achieved for the 25 and 50 g/L zeolite suspensions after about 30 minutes.

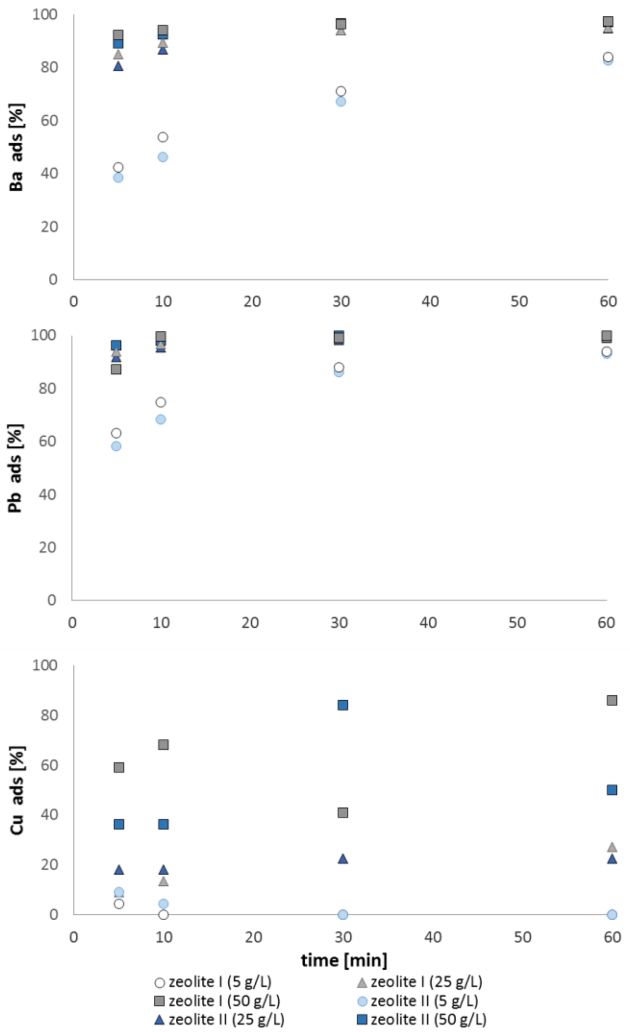

Figure 4: Removal of Ba, Pb, Cu in a mixed solution (all three metal ions together in a 10 mM NaCl) with low starting concentrations (5.2 mg/L Ba, 7.9 mg/L Pb, and 2.2 mg/L Cu).

Experiment III: Results of experiments with either zeolite I, chitosan, or magnetite-coated quartz sand as adsorbent material together with very high heavy metal (Pb, Ba, Cu) background concentrations (1 mM each, corresponding to 207.2 mg/L Pb, 137.3 mg/L Ba, 63.5 mg/L Cu) at various salinities (0.1, 1, 2 M NaCl) are presented in Figure 5. These results demonstrate that Ba was hardly removable from these solutions for all tested experimental conditions (Fig. 5). Only together with zeolite in 2 M NaCl about 5-10 % of the initial Ba were bound to the mineral. Copper removal worked best for salinities of 1 M NaCl. While for chitosan the removal increased over time (showing a Freundlich adsorption behaviour, which is characteristic for cation adsorption, for example on iron oxides or clay minerals.), it remained rather constant for zeolite (about 13-17 % removal, Fig.5). Cu adsorption was highest for chitosan. Altogether up to 48 % of the Cu were removed from the solution after 120 minutes. Magnetite proved at given conditions to be a not very good adsorbent material (< 8% removal of copper, < 20 % removal of Pb and hardly and Ba adsorption). In general, Pb removal was best for all three adsorbent materials. While for zeolites, time and salinity had only little effect on the adsorption (always between 8 and 17 %), chitosan showed again a Freundlich adsorption isotherm for Pb and Cu (up to nearly 60 % were removed from solution after 2 h in 1 M NaCl solution).

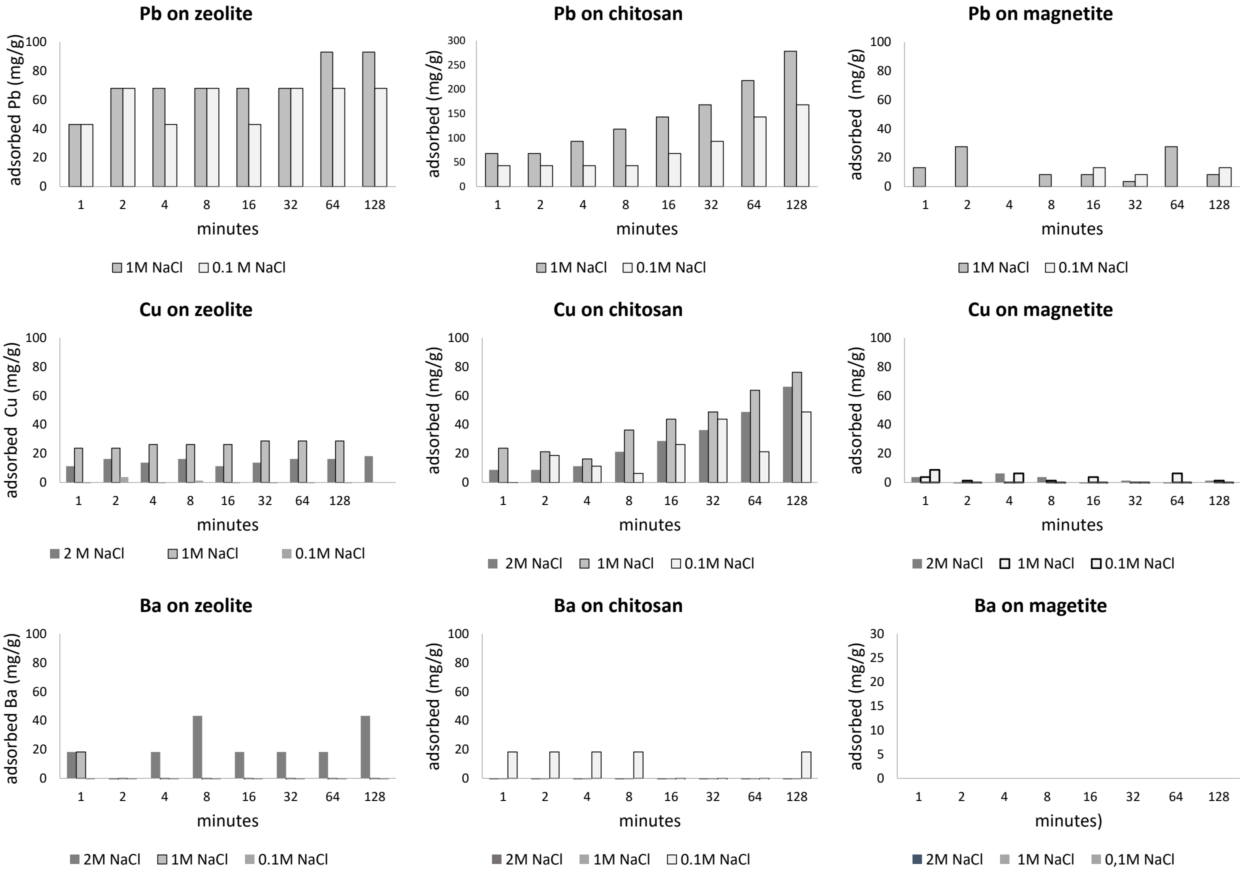

Figure 5: Amount of Cu, Pb, Ba (initial concentration each 1 mM) adsorbed to the three materials over time (2 h in total) at two (for Pb) or three (for Cu) different salinities.

The low adsorption capacity of magnetite (0-20 mg/g) might be due to the surface area that is too small or because of the solution conditions, because the experiments were performed aerobically, which might result in a partly oxidation of the iron (magnetite is a Fe(II)-, Fe(III) mineral). Dissolved oxygen might result in oxidation and hydrolysis of the Fe(II) part of Fe_3O_4 resulting in formation of Fe(III) hydroxides and simultaneously decreasing in pH by removing OH^- ions from the aqueous phase. At low pH values, however, cation adsorption on magnetite is very low (Cornell & Schwertmann, 1996) thus explaining the low metal removal in the experiments. Due to these observations, future experiments with magnetite will be carried out at strictly anoxic conditions.

4. CONCLUSIONS

This study aims at finding and defining materials that are able to bind unwanted components of a geothermal fluid to their surface and thereby removing them from the water thus preventing an oversaturation and precipitation of scaling minerals. The tested materials (zeolite, chitosan and magnetite-coated quartz) all showed capacities to remove some of the investigated metals Ba, Pb, and Cu. Especially at low initial metal concentrations, adsorption of Pb and Ba was nearly 100 % for zeolite. Lead could also be well removed from solutions even at higher concentrations and salinities. At these conditions (1 mM Pb, 1 M NaCl), up to 60 % of a 1 mM Pb solution (207 mg/L) was bound chitosan. In contrast, only little Ba was bound to the respective surfaces when added at high concentrations to the adsorbent material (not at all to magnetite and < 10 % to zeolite and chitosan).

Of the three tested materials chitosan showed highest adsorption capacities to bind Cu and Pb ions. The effect of salinity on the process is also relevant inasmuch as a medium salinity of 1 M NaCl resulted in highest metal adsorption. Ba adsorption was best on zeolite: at lower Ba concentrations up to 100 % were removed (20-70 mg/g). Another parameter that will be considered in further tests in the potential competition of Ca^{2+} that usually occurs in very high concentrations in saline brines with Ba^{2+} or other metals for sorption sites.

Although the binding of Ba and Pb to the chitosan was quite high and thus the material proofed to be most effective for removing these cations from solution, the reaction was relatively slow. This is not ideal, since in that case the adsorption material cannot directly be used as a filter and operated in a flow-through system. Moreover, the temperature stability of chitosan still needs to be investigated before application in a thermal water. After having performed these experiments at room temperature, static experiments will be carried out in a batch reactor at elevated temperatures. Further investigations about the use of the materials at geothermal-near conditions will be tested in a next step by applying them in the flow-through reactor (FluMoRe) that was adapted for the needed experiments, both, at static and dynamic conditions. Once the methods are successfully tested, their application in at a geothermal site will be prepared. Care needs to be taken when deciding which adsorbent materials should be tested for certain metals at given conditions. Modeling of results will help to predict metal removal capacities in future.

Eventually it is planned to test the adsorbent materials within a bypass of a geothermal power plant. As tested before in the static and dynamic reactor experiments the adsorbent will be either added into a reaction container to react for a given time before a filter unit can be connected or the adsorbent will be installed directly in a filter unit “metal cation filter”. Besides removing unwanted metals, this method could also be applied for removing valuable metals, such as lithium from the geothermal brine. More experiments are needed to test their efficiency on binding those metals.

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REFERENCES

Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. *Water research*, **33**(11), 2469-2479.

Çelik, A., Koç, G., Erdoğan, E., Shahwan, T., Baba, A. and Demir, M.M., 2017. Use of electrospun fiber mats for the remediation of hypersaline geothermal brine. *Desalination and Water Treatment.*

Schwertmann, U. and Cornell, R.M., 2000. Iron oxides in the laboratory (Vol. 2). Weinheim: Wiley-Vch.

Erdem E, Karapinar N, Donat R. The removal of heavy metal cations by natural zeolites. *Journal of colloid and interface science*, **15** (2004), 309-14.

Lasheen, M.R., El-Sherif, I.Y., Sabry, D.Y., El-Wakeel, S.T. and El-Shahat, M.F., 2014. Removal and recovery of Cr (VI) by magnetite nanoparticles. *Desalination and Water Treatment*, **52** (34-36), 6464-6473.

Milsch, H., Giese, R., Poser, M., Regenspurg, S. and Kranz, S., Integrated Fluid-chemical Monitoring Systems for Geothermal Applications. *Proceedings*. World Geothermal Congress Melbourne (Australia) (2015).

Moshoeshoe M, Nadiye-Tabbiruka MS, Obuseng V. A review of the chemistry, structure, properties and applications of zeolites. *Am. J. Mater. Sci.*, **7**(5) (2017), 196-221.

Parkhurst, D. L., Appelo, C. A. J. (1999): User's guide to PHREEQC (Version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemi-cal calculations. Hg. v. U.S. Geological Survey (Water-Resources Investigations Report, 99-4259.

Regenspurg, S., Feldbusch, E., Byrne, J., Deon, F., Driba, D.L., Henninges, J., Kappler, A., Naumann, R., Reinsch, T. and Schubert, C., 2015. Mineral precipitation during production of geothermal fluid from a Permian Rotliegend reservoir. *Geothermics*, *54*, pp.122-135.

Regenspurg S, Driba DL, Zorn C. Formation and significance of laurionite in geothermal brine. *Environmental Earth Sciences*. **75** (10) (2016), 865.