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Laboratory Leaching Tests to Investigate Mobilisation of Metals within Engineered Geothermal Reservoirs

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ABSTRACT

Within engineered geothermal systems (EGS), the recirculation of hot fluids would facilitate the recovery of dissolved metals, as well as energy, in a surface plant. Potentially, this would generate a second source of revenue, and thus increase the economic attractiveness of EGS development. This concept is the focus of the 'Combined Heat, Power and Metal extraction from ultra-deep ore bodies' project (CHPM2030, https://www.chpm2030.eu), where the potential for exploiting hot, metal-bearing geological formations at depths greater than 3 km has been investigated. The strategic objective of the CHPM2030 project is to develop a novel technological solution to both make geothermal energy more attractive and to reduce Europe's dependence on the import of metals and fossil fuels.

A key aspect of such a scheme is that sufficient quantities of metals can be mobilised and transported to make the process economic, and critical factors underpinning this are the rates and magnitudes of metal release in the reservoir zone. Laboratory experiments simulating in-situ conditions, using batch and flow-through reactors, have been used at up to 250°C and 300 bar to provide well-constrained data to help to understand and quantify these processes. Such experiments also allow testing of different fluid compositions in order to ascertain if there are specific additives that may improve the metal recovery process. Furthermore, evidence for the degree of leaching may allow assessment of whether it might increase system performance over time - through, for example, silicate and ore mineral dissolution and consequent permeability enhancement.

We report a series of leaching tests on rocks from Cornwall, UK, that used a variety of leaching fluids over a range of temperature, pressure and timescale. Increases were found in the concentration of many metals and were broadly correlated with increasing temperature and acidity. It was also noted that the presence of suitable ligands also increased metal concentration in solution, including chloride ions and organics (e.g., acetic acid). Interpretation of solution chemistry involved grouping elements together, such as 'common' elements (less economic importance and higher occurrence), and 'at risk' (those having higher economic value defined by the European Union - also termed 'strategic' elements in the US). One of the highest concentrations of 'common' elements was lead (up to 870 ppm using solutions containing acetic acid in batch experiments) and up to 540 ppm in flow-through experiments. Notable concentrations of Fe and Zn are also present in leachates, due to enhanced dissolution of sulphide mineralisation in the samples. Significant concentrations of Al and Si were also found in some leaching solutions, indicating considerable dissolution of matrix silicates, such as quartz and mica, present in the samples. This could be desirable in terms of increasing reservoir permeability and opening flow paths, but if concentrations become too high there is an increased risk of precipitation due to saturation with secondary phases, which could clog fractures and inhibit fluid flow in a geothermal reservoir, and risk fouling boreholes or surface infrastructure. Notable was that dilute acetic acid solutions achieved relatively high concentrations of some metals, but comparatively low concentrations of Al and Si, so limiting the potential for the formation of potentially problematical precipitates. We recognise however, that full extrapolation to a natural setting will require consideration of groundwater chemistry, fluid migration pathways and residence times, variations in surface areas, and decreases in available metals over time, and ongoing work seeks to investigate this. The data gathered here suggests that, given sufficient characterisation of the mineralogy and fluid chemistry of deep geothermal systems, it may be possible to tailor the chemistry of leaching solutions to maximise metal recovery.

1. INTRODUCTION

The idea of using geothermal brines for mineral extraction has existed for decades, with lithium currently being an element of special interest (Dang and Steinberg, 1978; Duyvesteyn, 1992; Kesler et al., 2012). However, a wide spectrum of other elements may also be suitable for extraction (Bloomquist, 2006; Neupane and Wendt, 2017). Here we consider engineered geothermal systems (EGS), where recirculation of hot fluids would facilitate the extraction of dissolved metals, as well as energy, in a surface plant. This could generate an additional source of revenue, and thus increase the economic attractiveness of EGS development. This concept is the focus of the project 'Combined Heat, Power and Metal extraction from ultra-deep ore bodies' (CHPM2030, a European Union H2020-funded project), where the potential for exploiting hot metal-bearing geological formations at depths greater than 3 km has been investigated. The strategic objective of the CHPM2030 project is to develop a novel technological solution to make geothermal energy more attractive and to reduce Europe's dependence on the import of metals and fossil fuels (European Commission et al., 2017).

In the envisioned technology, an EGS is established within a metal-bearing geological formation at depths greater than 3 km (Figure 1). A key aspect of such a scheme is that sufficient quantities of metals can be mobilised and transported to make the process economic, and critical factors underpinning this are the rates and magnitudes of metal release. Laboratory experiments simulating in-situ conditions are a useful way to provide well-constrained data to help to understand these. Such experiments also allow testing of different fluid compositions in order to ascertain if there are specific additives that may improve the metal recovery process (Kilpatrick et al., 2017). Furthermore, evidence for the degree of leaching may allow assessment of whether it might increase system performance over time - through, for example, silicate and ore mineral dissolution and consequent permeability enhancement.

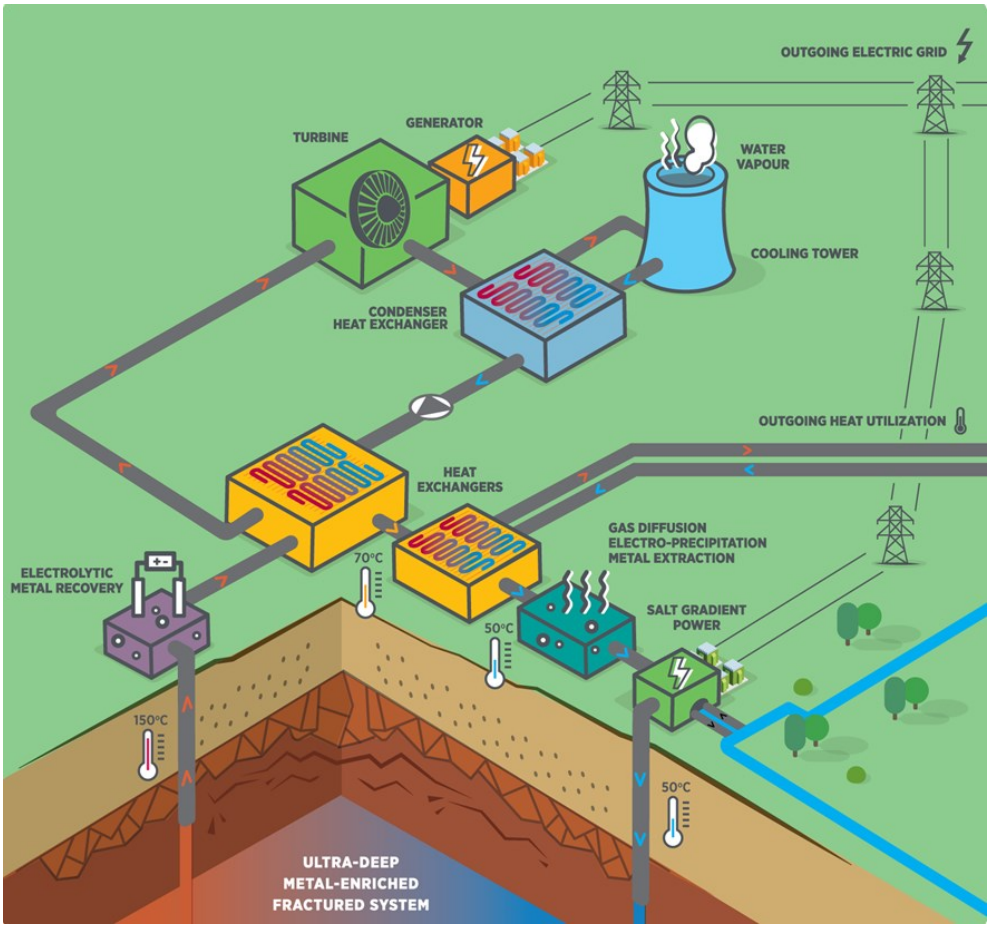


Figure 1: Schematic representation of the CHPM concept. The information presented here relates to the release of metals from the 'ultra-deep orebody' and into the recirculating geothermal fluid.

2. METHODS

Initial lower temperature experiments (not presented here) explored the leaching potential of various fluids, and the more promising of these were used to leach a wider range of mineralised samples under higher pressure/temperature conditions typical of those that might be expected at 3–4 km depth. Here we present results using rock samples reacted with fluids that were very benign (deionised water), to slightly aggressive (0.1 M acetic acid), to relatively aggressive (a mixture of 0.1 M hydrochloric acid [HCl] and 0.03M nitric acid [HNO_3]). Relatively simple solutions were used in our tests as we were studying the comparative behaviour of metals. However, the chemical composition, and especially salinity, of in-situ groundwater will be important, though there is a general lack of information on the chemistry of deep groundwaters. While strong acids clearly have more potential to dissolve rock and associated mineralisation, dissolution potential is not the only consideration. Also of importance is the potential impact on the reservoir, geothermal plant infrastructure, and the wider environment. There is thus a trade-off between these different aspects, and hence it is useful to investigate and compare the relative performance of a variety of potential leachants.

2.1 Materials

The solids used in the experiments comprise:

- Fracture-hosted, mixed sulphide mineralisation from Cornwall (UK): 87% quartz, 5% muscovite, 2% dolomite, 5% galena, minor albite, chlorite, pyrite, and sphalerite.
- Carbonate hosted lead-zinc mineralisation from Rudabánya (Hungary): 8% quartz, 2% calcite, 68% magnesite, 6% cerrusite, 1% sphalerite, 1% columbite, 11% barite, 2% magnetite, and minor dolomite.
- Porphyry sulphide polymetallic ore from Recsk (Hungary): 74% quartz, 5% calcite, 9% pyrite, 11% magnetite, minor albite, dolomite, and sphalerite.
- Mineralised skarn adjacent to Banatitic intrusions at Masca-Cacova Ierii (Romania): 22% dolomite, 49% pyrite, 27% magnetite, minor quartz, calcite, and barite.

Samples consisted of either massive mineralisation, or mineralised material together with some surrounding country rock. All samples were crushed, sieved, and cleaned to produce a 500-250 µm fraction free of fines, which was used for the experimental and analytical work. This fraction was cleaned to remove fines and surface impurities by repeated rinsing in acetone until the supernatant ran clear. These were then oven dried at 30°C.

2.2 Experimental methods

Batch and flow-through experiments were conducted at 70–250 °C; here we focus on the higher temperature runs (a summary of the lower temperature experiments is given elsewhere (Osvald et al., 2018)).

2.2.1 Batch experiments

Batch experiments were conducted at 100–200 °C in titanium reactors inside thermostatically-controlled, fan-assisted ovens (Bateman et al., 2013; Moyce et al., 2014; Rochelle et al., 2016). Into each was added 8.75 g of granulated rock and 350 ml of leaching solution, plus a magnetic stirrer bead. Fluids were sampled via titanium dip tube fitted with a PTFE filter (Figure 2). To minimise mechanical damage to the solid, a caged stirrer bead was used, and only activated for 2 minutes every 4 hours. Nitrogen gas was used to pressurise the experiments. At the end of each experiment as much of the solution as possible was removed prior to cooling. Once well below 100 °C, the vessel was slowly depressurised, dismantled, and reacted rock grains recovered for subsequent analysis. Experiments ran for 600–1000 hours.

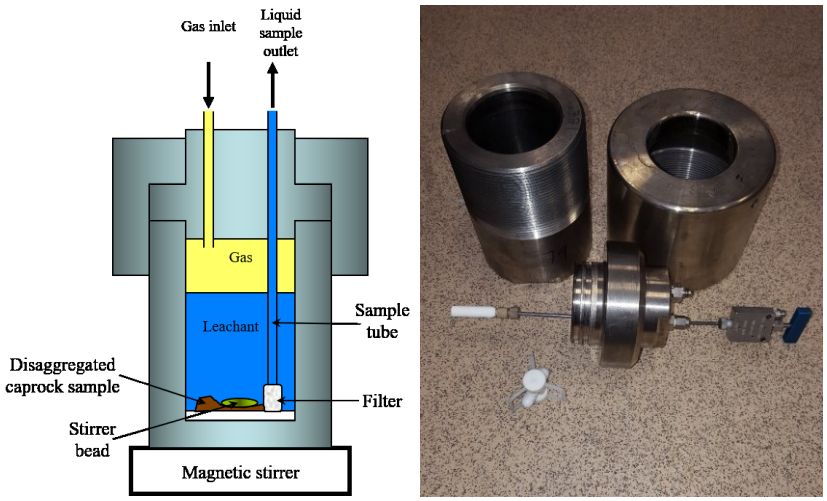


Figure 2: Schematic diagram and photograph of a titanium batch reactor.

2.2.2 Flow-through experiments

Leaching processes were also investigated under continuous flow conditions using a stainless steel HPLC column reactor (250 mm long, 21.2 mm inner diameter) containing 150 g of granulated rock sample. Pressure inside the column was maintained by an Econ Kappa 10 HPLC pump and a back-pressure regulator fitted at the outflow of the column (Figure 3). A digital thermostat allowed heating bands attached to the column to maintain temperatures to ±1 °C. Leaching tests operated at 200–250 °C and 250 bar. Flow was 0.5 ml per minute, giving a residence time of 30–50 minutes.



Figure 3: Flow-through reactor (left) and temperature control on top of the HPLC pump used (right).

3. RESULTS

Data are summarised in Figure 4, which shows the sum of mobilised 'common' elements at approximately 80 ppm, 300 ppm and 213,000 ppm for leaching using deionised water, 0.1 M acetic acid and 0.13 M mineral acid respectively. The large increase in total dissolved elements in the latter is largely due to silica (approximately 211,000 ppm) from the dissolution of silicate minerals. Whilst the dissolution of these may enhance flow paths in the geothermal reservoir through increased permeability, it may also enhance mineral precipitation in surface infrastructure during the depressurisation and cooling of the geothermal fluids.

In terms of 'traditional' ore metals, there were notable increases in dissolved Ni, Pb, and Zn as more acidic solutions were used. These (together with the increases in Fe) suggest sulphide mineral dissolution. Leaching was most rapid in the first few tens of hours for both types of experiments, and in the batch experiments slowed towards steady-state rates after several hundred hours of reaction. Relatively fast reactions would benefit the CHPM concept, as they would maximise metal concentrations in solution even with relatively short fluid residence times in the geothermal reservoir. However, on a reservoir scale this would mean that a formation with limited 'ore minerals' will deplete over time, and thus metal extraction would be most efficient early on in an extraction project, with returns likely to decrease on the medium to long term (Szanyi et al., 2017). It is thus important to understand how leaching rates will vary over time.

Total concentrations of 'at risk' elements (elements which, due to value or scarcity, are relatively desirable) are approximately 50 ppb, 830 ppb, and 8500 ppb for leaching using deionised water, 0.1 M acetic acid and 0.13 M HCl/HNO_3, respectively (Figure 5). Again, there is a strong relationship between acidity and the total amount of mobilised elements. The results indicate, however, that even a relatively mild leachant, such as acetic acid, can significantly increase leaching potential. In this case, a switch from deionised water to acetic acid generated a 20-fold increase in dissolved load of the selected 'at risk' elements.

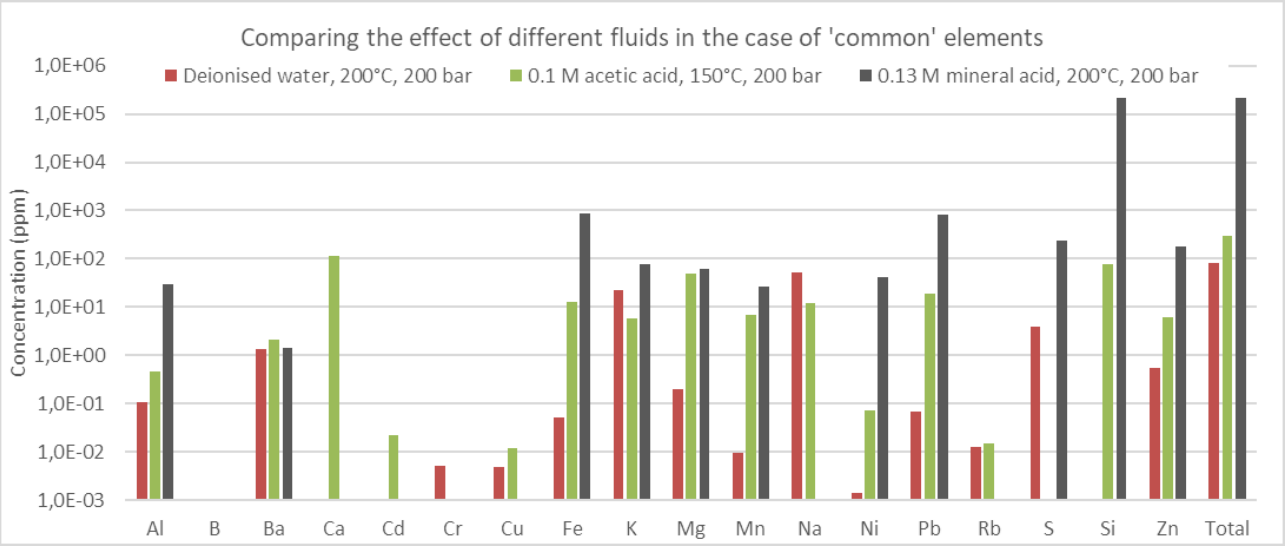


Figure 4: Comparison of the effectiveness of different fluids for 'common' elements (data from batch experiments, concentration values in ppm).

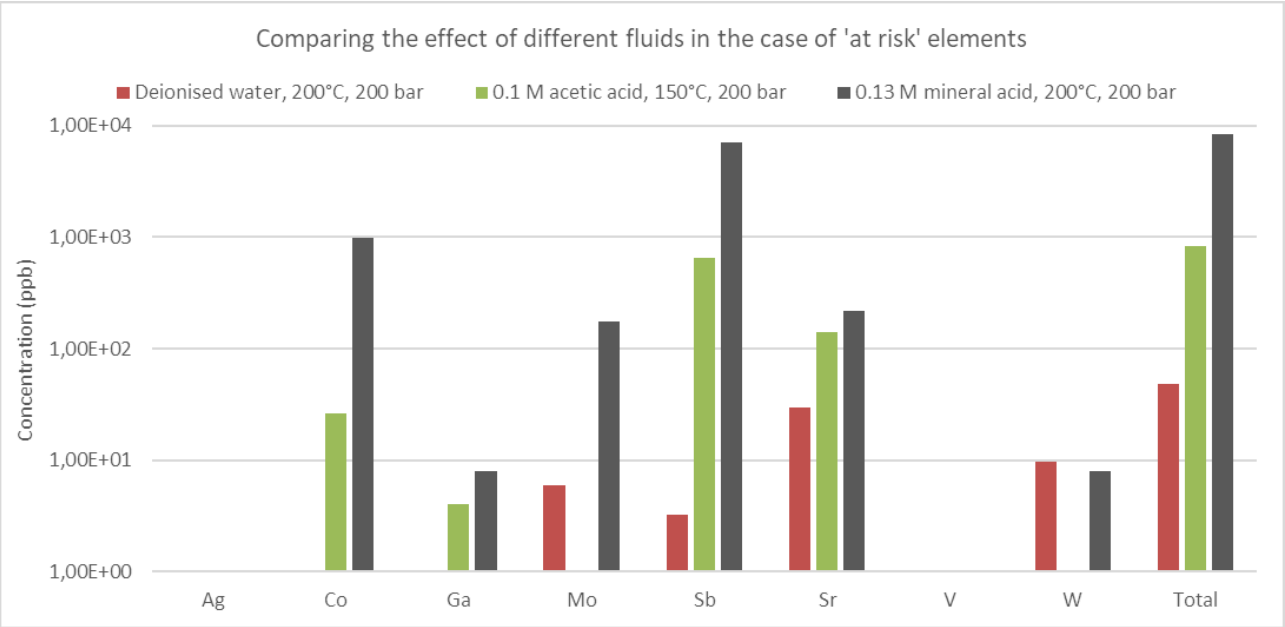


Figure 5: Comparison of the effectiveness of different fluids for a selection of 'at risk' elements (data from batch experiments, concentration values in ppb).

4. CONCLUSIONS

Recovery of metals from recirculating fluids has been proposed as a way to improve the economics of operating engineered geothermal systems. Fundamental to this is an understanding of metal release processes, and we have conducted preliminary batch and flow-through laboratory leaching tests at up to 250 °C and 300 bar to investigate the potential for metal mobilisation under in-situ conditions. A range of mineralised rocks from Cornwall (UK), Rudabánya and Recsk (Hungary), and Masca-Cacova Ierii (Romania) were reacted with a range of leaching fluids, including deionised water, dilute acetic acid, and dilute HCl/HNO_3, for up to 1000 hours.

Increases were found in the concentration of many metals and were broadly correlated with increasing temperature and acidity. It was also noted that the presence of suitable ligands also increased metal concentration in solution, including Cl^- and especially organics (e.g., acetic acid). Interpretation of solution chemistry involved grouping elements together, such as 'common' elements (less economic importance and higher occurrence), and 'at risk' (those having higher economic value defined by the European Union - also termed 'strategic' elements in the US). One of the highest concentrations of 'common' elements was lead (up to 870 ppm with acetic acid in batch experiments) and up to 540 ppm in flow-through experiments. Notable concentrations of Fe and Zn are also present in leachates, due to enhanced dissolution of sulphide mineralisation in the samples.

Significant concentrations of Al and Si were also found in some leaching solutions, indicating considerable dissolution of matrix silicates present in the samples. This could be desirable in terms of increasing reservoir permeability and opening flow paths, but if concentrations become too high there is an increased risk of precipitation, which could clog fractures and inhibit fluid flow in a geothermal reservoir, and risk fouling boreholes or surface infrastructure. Notable was that dilute acetic acid solutions achieved relatively high concentrations of some metals, but comparatively low concentrations of Al and Si and several of the more desirable metals. The data gathered here suggests that, given sufficient characterisation of the mineralogy and fluid chemistry of deep geothermal systems, it may be possible to tailor the chemistry of leaching solutions to maximise metal recovery.

5. ACKNOWLEDGEMENT

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