

Batch and flow-through leaching of different metallic rocks under geothermal reservoir circumstances

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ABSTRACT

The European Union's Horizon 2020 project, 'Combined Heat, Power and Metal extraction' (CHPM2030), aims to develop a novel technology combining geothermal energy utilisation with metal extraction in a single interlinked process. To improve the economics of geothermal energy production, this project investigates possible technologies for exploiting metal-bearing geological formations with geothermal potential at depths of 3–4 km or deeper. This could enable co-production of energy and metals in the future, allowing for the mining of deep ore bodies, particularly those of critical metals, alongside power production while minimising environmental impacts.

Laboratory leaching experiments were conducted herein as part of this project. These experiments involved testing a variety of potential leaching fluids with various mineralised samples to assess leaching effectiveness. Ground mineralised rock samples were investigated under conditions similar to those geothermal reservoirs (e.g. 250 bar, 250°C). Each experiment was conducted using one of the wide ranges of fluids for a relatively long time (up to 720 h) in batch reactors, and selected fluids were used in a flow-through reactor using a shorter contact time (0.6 h). To ensure possible application to a real geothermal reservoir, only environmentally friendly fluids were considered, such as deionised (DI) water, acetic acid and dilute mineral acid (a mixture of hydrochloric acid and nitric acid).

The main findings of this study include fast reaction times, which imply that steady-state fluid compositions were attained within the first few hours of reaction and the mobilisation of Ca, Cd, Mn, Pb, S, Si and Zn enhanced. Some critical elements, such as Co, Sr and W, were also found in notable concentrations during fluid-rock interactions. However, the amount of these useful elements were considerably lesser than those of the other common elements such as Al, Ca, Fe, K, Mg, Mn, Na, Pb, S, Si and Zn. Although dissolved metal concentrations increased during the tests, some remained low; these low metal concentrations will present technical challenges for metal extraction.

However, we are working towards obtaining actual deep fluids to better constrain parameters, such as salinity, that also influence metal solubility.

1. INTRODUCTION

The idea of using geothermal brines for mineral extraction has existed for decades. Lithium is currently an element of interest for mineral extraction (Dang and Steinberg 1978, Duyvesteyn 1992, Kesler et al. 2012); however, a wide spectrum of other elements may also be suitable (Bloomquist 2006, Neupane and Wendt 2017). Herein, engineered geothermal systems (EGS) are considered, which use recirculated hot fluids to facilitate the extraction of dissolved metals and energy in a surface plant. Extracting energy provides a second revenue source, thus increasing the system's economic attractiveness. This concept is the focus of the European Union's Horizon 2020 project, 'Combined Heat, Power and Metal extraction' (CHPM2030), which investigates the potential for exploiting hot metal-bearing geological formations deeper than 3 km. The strategic objective of the CHPM2030 project is to develop a novel technological solution that makes geothermal energy more attractive and reduces Europe's dependence on metal and fossil fuel imports (European Commission 2017).

The envisioned scheme has an EGS established within a metal-bearing geological formation deeper than 3 km. A key aspect of such a scheme is that sufficient quantities of metals can be mobilised and transported to the surface (Hartai et al. 2016). In situ laboratory experiments using batch or flow-through reactors can provide well-constrained data to elucidate mobilisation processes and solution behaviours. Such experiments also allow testing of different fluid compositions to ascertain whether specific additives can improve the metal recovery process (Kilpatrick et al. 2017). Furthermore, evidence for the degree of leaching from such experiments may allow assessing whether leaching through dissolution and consequent permeability enhancement might increase system performance over time.

2. METHODS

Initial low-temperature experiments conducted by Kilpatrick et al. (2017) and Osvald et al. (2018) explored the leaching potentials of various fluids. Fluids showing more promise were used to leach a wider range of mineralised samples at higher pressures and temperatures that might be expected at depths of 3–4 km. Herein, results from rock samples reacted with very benign (deionised (DI) water), slightly aggressive (0.1 M acetic acid) and relatively aggressive (dilute mineral acid: mixed 0.01 M hydrochloric acid and 0.003 M nitric acid) fluids are presented. Relatively simple solutions were used in our tests because comparative behaviours of metals were being analysed. However, the chemical composition (particularly salinity) of in situ groundwater is deemed important although the deep groundwater chemistry remains unexplored. Mineral acids, such as nitric or hydrochloric acid, clearly have a greater potential to dissolve rock and associated minerals; however, there

are considerations other than a fluid's dissolution potential, such as the fluid's potential effects on the reservoir, geothermal plant infrastructure and the overall environment. Thus, a trade-off exists between these different aspects, making it useful to investigate and compare the relative performance of a variety of potential leachants.

2.1 Materials

To cover the widest possible range of reservoirs, different mineralised rocks were collected and crushed to obtain a <500- μm powdered fraction. We then sieved this fraction to produce a 500–250- μm fraction for the experimental and analytical work. We repeatedly rinsed this fraction in acetone until the supernatant ran clear to remove fines and surface impurities and dried these 'washed' samples in an oven at 30°C. Table 1 shows the composition of each sample.

Table 1: Major geological and mineral properties of the samples

Sample ID	Sample locality	Geological setting	Summary of bulk mineralogy as determined via X-ray diffraction
HTLMix	Herodsfoot, SW England	Baked sediments with partial quartz vein	87% quartz, 5% muscovite, 2% dolomite, 5% galena, minor albite, chlorite, pyrite and sphalerite
HTL315	South Caradon, SW England	Mainstage mineralisation, associated with granite bodies	70% quartz, 7% schorl, 5% chlorite, 2% calcite, 10% pyrite, 5% arsenopyrite, minor greigite and biotite
HTL319	Cligga Head, SW England	Tin–tungsten mineralisation, associated with granite bodies	88% quartz, 2% muscovite, 3% cassiterite, 3% columbite and 4% ferberite
HTL321	Masca-Cocovaleni, Romania	Mineralised skarn country rock	22% dolomite, 49% pyrite, 27% magnetite, minor quartz, calcite and barite
HTL322	Rudabánya, NE Hungary	Carbonate hosted lead-zinc mineralisation	8% quartz, 2% calcite, 68% magnesite, 6% cerrusite, 1% sphalerite, 1% columbite, 11% barite, 2% magnetite and minor dolomite
HTL324	Recsk, NE Hungary	Porphyry sulphide polymetallic ore	74% quartz, 5% calcite, 9% pyrite, 11% magnetite, minor albite, dolomite and sphalerite

2.2 Experimental methods

Herein, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Rb, S, Si and Zn have the highest concentration. The economic value of these elements is debatable because of their limited utility or wide availability and are thus referred to as 'common' elements. We selected elements with higher economic value and lower concentrations, such as Ag, Co, Ga, Mo, Sb, Sr, V and W, as desirable and referred to them as 'at risk' elements based on the evaluation by European Commission et al. (2017).

Batch experiments: Batch experiments were conducted at 100°C–200°C and 200–250 bar in titanium reactors inside thermostatically controlled, fan-assisted ovens (Bateman et al. 2013, Moyce et al. 2014, Rochelle et al. 2016). We added 8.75 g of granulated rock and 350 ml of leaching solution into each reactor along with a caged magnetic stirrer bead. Fluids were sampled using a titanium dip tube, and the caged stirrer bead was only activated for 2 min every 4 h to minimise mechanical damage to the solids. Nitrogen gas was used to pressurise the experiments. At the end of each

experiment and prior to cooling, maximum possible amount of solution was removed. Once the temperature reached well below 100°C, the vessel was slowly depressurised and dismantled; then, the reacted rock grains were recovered for subsequent analysis. Experiments were conducted for 600-1000 h. Batch experiments were conducted using DI water, acetic acid (in 0.1 M concentration) and mineral acid (a mixture of 0.13 M HCl and 0.013 M HNO₃) as leaching solutions on samples HTLMix, HTL315, HTL319, HTL321 and HTL324 at 70°C, 100°C, 150°C and 200°C at 200 bar and at 1 bar for experiments conducted at 70°C.

Flow-through experiments: Leaching processes were also investigated under continuous flow conditions using a stainless steel high-performance liquid chromatography (HPLC) column reactor (250-mm long, 21.2-mm inner diameter) containing 150 g of granulated rock sample. Pressure inside the column was maintained using an Econ Kappa 10 HPLC pump and a back-pressure regulator fitted at the column outflow. A digital thermostat was used to control heating bands attached to the column to maintain temperatures within $\pm 1^\circ\text{C}$ of target temperatures. Leaching tests were conducted at 200°C–250 °C and 250 bar. Leaching solution flow was 0.5 ml per minute, which yielded a 30–50-min residence time for an 8-h experiment. The flow-through experiments were conducted using DI water and 0.1 M acetic acid on samples HTL315, HTL139, HTL321, HTL322, HTL324 and HTLMix at 200°C and 250°C under 250-bar pressure.

3. RESULTS AND DISCUSSION

Figure 1 shows the total amount of ‘common elements’ mobilised in samples of approximately 80, 300, and 213,000 ppm for leaching experiments using DI water, 0.1 M acetic acid and 0.13 M mineral acid (a mixture of 0.01 M hydrochloric acid and 0.003 M nitric acid), respectively. The large increase in the amount of total dissolved elements in the latter is largely caused by silica (~211,000 ppm) obtained from the dissolution of silicate minerals. Although the dissolution of silicates may enhance flow paths in geothermal reservoirs by increasing permeability, it can also enhance mineral precipitation in surface infrastructure during the depressurisation and cooling of the geothermal fluids.

Figure 2 shows the total concentrations of ‘at risk’ elements (those that are relatively desirable due to value or scarcity) of approximately 50, 830, and 8500 ppb for leaching experiments using DI water, 0.1 M acetic acid, and 0.13 M mineral acid, respectively. Acidity and total amount of mobilised elements are strongly correlated; however, our results indicate that even a relatively mild leaching fluid, such as acetic acid, which has a pH of ~2.8, can considerably increase the leaching potential. In this case, switching from DI water to acetic acid generated a 20-fold increase in the dissolved load of ‘at risk’ elements. Leaching with acetic acid resulted in moderate ‘at risk’ metal concentrations and considerably lower Al and Si concentrations, which suggests that acetic acid is a viable leaching option and provides a good compromise between the release of useable metal and risk of scaling. Additionally, using mineral acids as leaching solvents could be more challenging in geothermal systems due to difficulties in transporting, handling and storing mineral acids as well as environmental issues related to their use. Acetic acid was more effective than DI water but less effective than mineral acid in terms of both dissolved ‘at risk’ element concentrations and range of elements leached in detectable concentrations.

In terms of ‘traditional’ ore metals, we observed notable increase in the concentration of dissolved Ni, Pb and Zn, resulting from more acidic solutions. Increase in the concentrations of these elements together with increase in Fe concentration suggests sulphide mineral dissolution. Leaching was most rapid in the first few tens of hours in both types of experiments. In the batch experiments, leaching slowed considerably after several hundred hours. Relatively fast reactions would benefit the CHPM2030 concept as they would maximise metal concentrations in solution with relatively short fluid residence times in geothermal reservoirs. However, on a reservoir scale, this would mean that formations containing limited ‘ore minerals’ would deplete over time, implying that metal extraction would be most efficient early in an extraction project and returns likely decreasing over longer terms (Szanyi et al. 2107). Thus, it is important to understand how leaching rates vary over time.

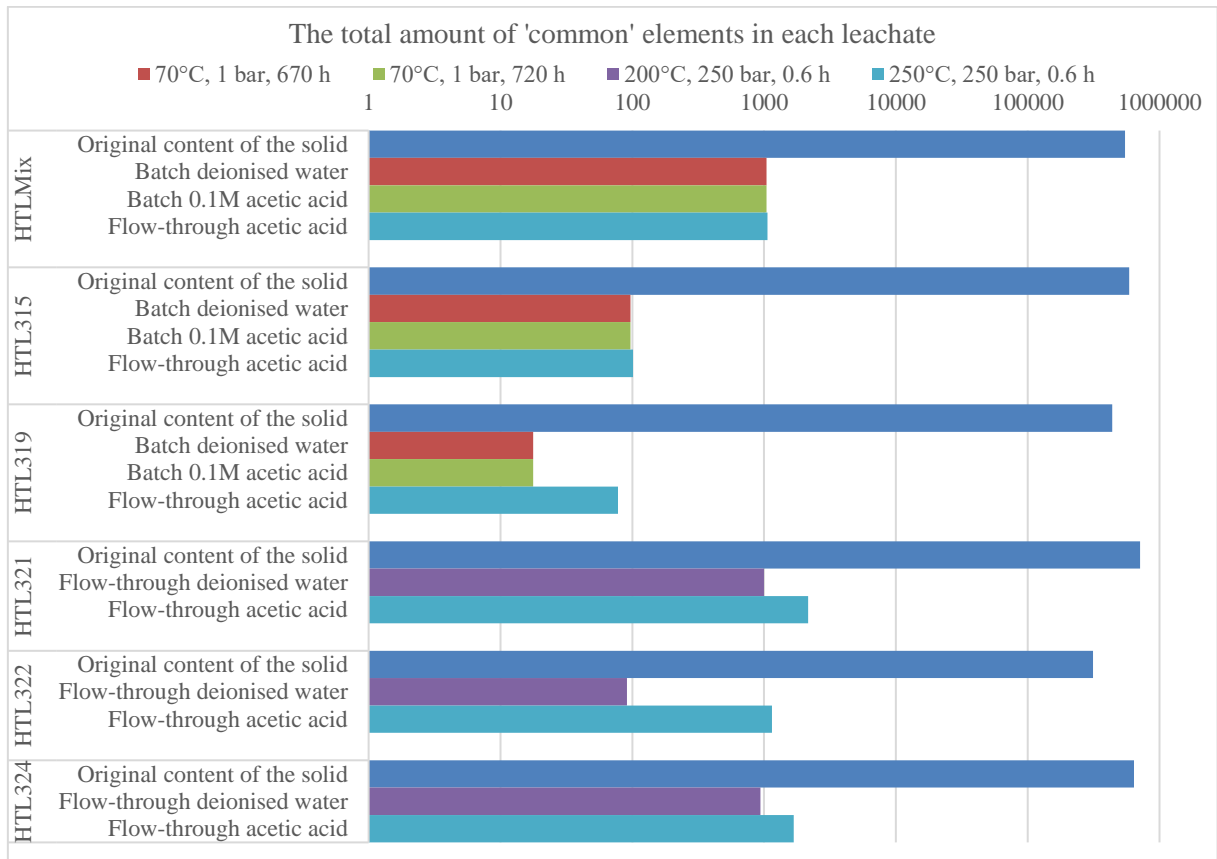


Figure 1: Summarising chart of detected 'common' elements during each experiment. Concentrations are denoted in ppm

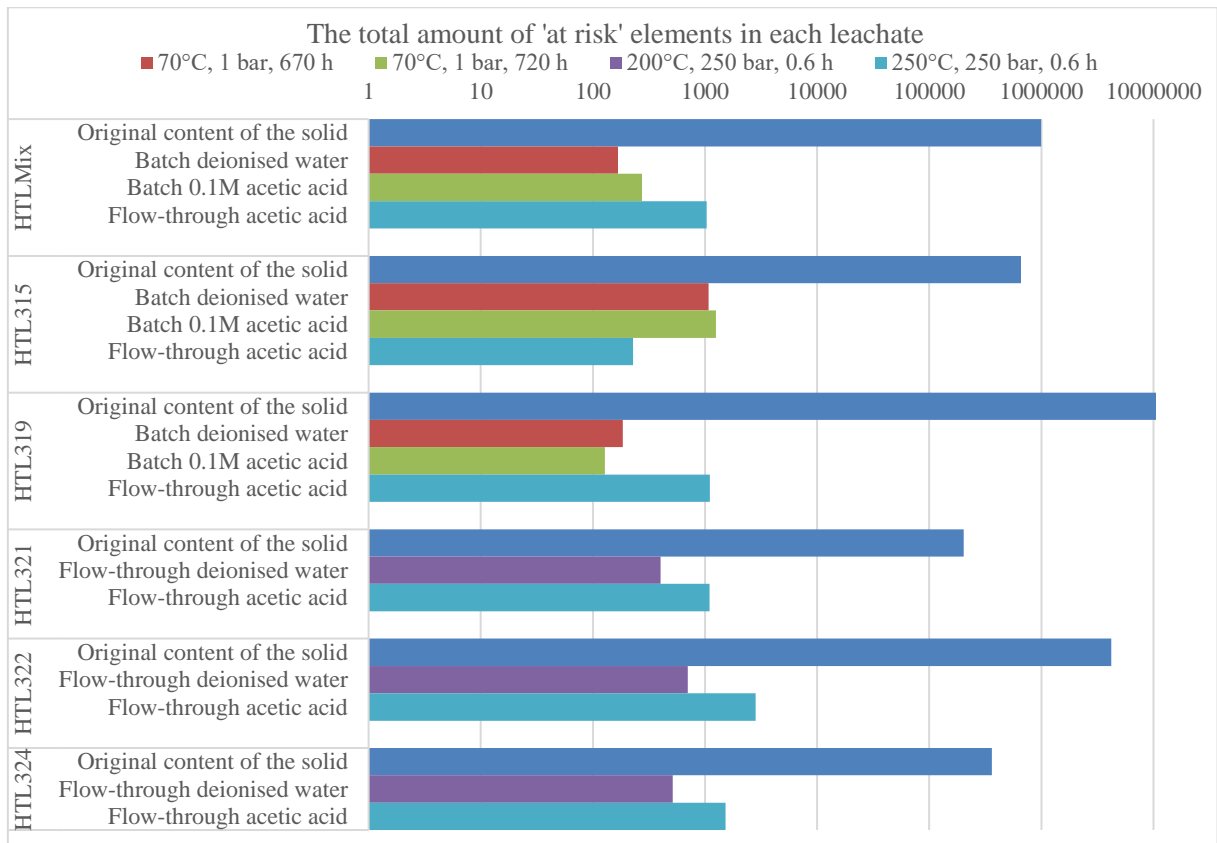


Figure 2: Summarising chart of detected 'at risk' elements during each experiment. Concentrations are denoted in ppb

4. CONCLUSIONS

Laboratory batch and flow-through leaching tests were performed at 70°C–250°C and 1–250 bar; these conditions were similar to those in an average 3-km-deep geothermal reservoir. Reactions under these laboratory conditions yielded reasonable concentrations of a wide range of mobilised elements. Detected elements were grouped as common elements, which have less economic importance and higher occurrence in both the solid samples and the produced leachates, and ‘at risk’ elements, which have higher economic value and lower supply.

Recovering metals from recirculating fluids has been proposed to improve the economics of operating geothermal systems, for which the metal release processes must be clearly understood. Herein, we conducted preliminary batch and flow-through laboratory leaching tests at up to 250°C and 250 bar to simulate metal mobilisation potential under in situ conditions. The concentrations of many metals increased, which broadly correlated with increasing temperature and acidity. The presence of suitable ligands, such as Cl^- , particularly organic acid (e.g. acetic acid), also increased the solution metal concentrations. One of the highest ‘common’ element concentrations was Pb at up to 870 ppm with acetic acid in batch experiments and up to 540 ppm in flow-through experiments. Notable Fe and Zn concentrations are also present in leachates because of the 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 sample matrix silicates such as quartz and mica. This dissolution could be desirable in terms of increasing reservoir permeability and opening flow paths; however, excessively high concentrations increase the risk of precipitation due to saturation with secondary phases. This precipitation could clog fractures, inhibiting fluid flow in a geothermal reservoir and risk fouling boreholes or surface infrastructure. Notably, dilute acetic acid solutions achieved relatively high concentrations of some metals but comparatively low concentrations of Al and Si, which limits the potential for forming potentially problematic precipitates. However, we recognise that full extrapolation to a natural setting will require considering groundwater chemistry, fluid migration pathways and residence times, surface area variations and decreases in available metals over time. These factors will be considered in our ongoing investigations. The data gathered herein suggest that given sufficient characterisation of deep geothermal system mineralogy and fluid chemistry, leaching solution chemistry can be tailored to maximise metal recovery.

The highest concentration of a single ‘at risk’ element was a 1070-ppb Co concentration in batch reactors using acetic acid and a 2840-ppb Sr concentration in the

flow-through setup using acetic acid. Sr, Co, W and Mo were detected in the abundance during all leaching tests, which is a good motivation towards further experiments because W and Co have the European Union’s highest economic risk ratings.

Leaching reactions using reasonably mild and environmentally acceptable fluids can dissolve considerable amounts of silicate minerals and other elements of interest. Given proper conditions within a geothermal reservoir (high temperature and pressure and sufficient available surface area), fast reaction rates are promising for metal recovery potential. Future work and technological development are still needed to practically recover raw materials from geothermal fluids because concentrations desired for extraction tend to be higher than those achieved in this study. These results are intended to be scaled up to reservoir scale for calculating likely achievable dissolved loads given reaction rates and solubility of the various elements involved. In this study, the first steps were taken to ensure the sustainability of the proposed technology; further investigations, advances in other technologies and a full life cycle assessment study must follow.

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