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**Investigating metal leaching potential under  
geothermal reservoir circumstances with special focus  
on tungsten**

DOCTORAL THESES

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## INTRODUCTION AND AIMS

Geothermal energy is an alternative and – with responsible utilization – renewable energy resource, which is based on the inner heat of the Earth. Its exploitation is financially intensive, the risk of failure is highest at the early stages of development, due to data availability. To improve the economics of geothermal energy, not only the production of heat and electricity, but the potential to extract elements from the geothermal brine received attention. The extraction of lithium became the most popular.

The production of strategic metals is necessary for the sustainable development of the European Union. Producing such elements within Europe would decrease its dependency on import. Critical elements, required for the technoeconomic development, has been evaluated and ranked based on their supply risk. The currently available and extractable raw materials were also taken into account. A list was created, ranking raw materials on economic importance. Tungsten was on top of the list due to its importance and critical accessibility.

The aim of my doctoral research was to investigate metal leaching potential in laboratory under geothermal reservoir circumstances. Two types of experimental setups were used: Batch, where fluid:rock ratio was relatively high, the experiments were run up to 1000 hours. The complementary to these were flow-through reactions, where fluid:rock ratio was low, contact time was maximum 3 hours. Six different rock sample and two isolated tungsten minerals (and the mixture of these minerals) were reacted on different temperature (from 70°C to 300°C) and pressure (1 bar to 300 bar) with deionized water, acetic acid, a mixture of acids and sodium hydroxide.

After a broader spectrum of solids and fluids, tungsten was in my focus. Tungsten is a metal with the highest melting point of all elements (except carbon), as well as the highest atomic weight and density of all metals, making it a widely used metal with numerous industrial, civilian and military applications. China currently accounts for 82 % of the total global conventional extraction of tungsten, with the next closest producers being Vietnam (6 %), Russia (2 %) and Canada (2 %). Tungsten is mined throughout Europe, with mines in the United Kingdom, Austria, Portugal and Spain, but the supply is very limited, accounting for approximately 2.7 % of global production.

The potential of tungsten mobilization with environmentally friendly fluids (deionized water, acetic acid, dilute mixture of acids and sodium hydroxide) was explored by performing high-temperature flow-through experiments. To isolate the effect of each minerals, first pure

tungsten minerals (scheelite and ferberite) were used, later the mixture of these minerals with the ratio of 1:1.

## **EXPERIMENTAL METHODS**

Laboratory investigations were conducted in batch and flow-through experimental setup. During batch reactions fluid and ground rock samples in the ratio of 40:1 were reacted at 250°C and at 200 bar. pressure. Experiments were run for 600-1000 hours. To investigate the effect of a continuous flow, a custom built flow-through reactor was used with external heating. During flow-through experiments solid samples and fluid could react on 300°C temperature and 300 bar pressure at the same time. These circumstances correspond to the temperature and pressure of an average geothermal reservoir at 3 km depth.

As a result of the reactions with rocks in the laboratory, reasonable concentrations of a wide range of elements could be mobilized. Detected elements were grouped as “common” and “at risk” elements. Selected common elements have less economic importance and higher occurrence (in both the solid samples used and the produced leachates), while selected at risk elements have higher economic value, and lower supply security.

After investigating a wide range of rocks and fluids, based on international ranking of strategic raw materials, tungsten – as Europe’s highlighted critical element – was in the focus of my research. Ferberite (iron tungstate) and scheelite (calcium tungstate) isolates were reacted with selected fluids, in order to explore tungsten leaching potential. My goal was to investigate the potential of tungsten leaching and mobilization in an EGS. For this purpose a continuous flow-through externally heated pressure vessel was used to study fluid–rock interactions under various geothermal reservoir conditions. Tungsten minerals were leached with deionized water, acetic acid, mineral acid and sodium hydroxide at 200°C, 250°C and 300°C temperature, under 250-280 bar pressure with 0,5 ml/min and 1 ml/min flow rate.

## **SUMMARY OF NEW SCIENTIFIC RESULTS**

**T1. I demonstrated that various elements which are critical for the European Union could be mobilised from rock samples under geothermal reservoir circumstances in laboratory, in batch and in flow-through experimental setup, too.**

During leaching experiments in laboratory, I successfully mobilised common (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Rb, S, Si and Zn) and critical (Ag, Co, Ga, Mo, Sb, Sr, V and W) elements from uniformly ground rock samples. I reacted deionised water, acetic acid and mineral acid with solid samples between 200°C and 300°C temperature, around 250-300 bar pressure in batch and in flow-through experimental setup. The leachates from such reactions contained total 50 ppb critical elements with deionised water, 830 ppb with acetic acid and 8500 ppb with mineral acid. There is a strong relation between acidity and the concentration of mobilised elements.

**T2. I proved that fluids in environmentally acceptable concentration are capable to mobilise economically promising amount of material.**

In my experiments I used reasonably mild and environmentally acceptable fluids, in lower concentration than it is approved for the maintenance and repair works of a geothermal well (0,1 M acetic acid, which is not stronger than the household vinegar and 0,13 M mineral acid). I discovered that during the flow-through experimental setup Li mobilised in 500 ppb concentration in approximately 30 minutes of contact time. Besides lithium silicon (213000 ppm with mineral acid at 200°C temperature under 200 bar pressure), lead (805 ppm) and aluminium (209ppm) dissolved in larger quantity, but their economic importance is questionable.

I managed to mobilise cobalt (979 ppb), antimony (7100 ppb) and tungsten with mineral acid at 200C, all these elements are identified as critical elements by the EU. If this happens in a geothermal system with 3500 m<sup>3</sup>/day (40 l/s) flow rate, then the amount of produced metal is on the order of “kg/day”. To harness this potential, the efficiency of the metal extraction technology from geothermal brines is a key.

**T3. It is favourable to use a mild acid (such as acetic acid) in low concentration rather than a strong acid (mixture of HNO<sub>3</sub> and HCl) in low concentration for mobilising metals from rock samples.**

The huge increase in total dissolved elements is largely due to the previously mentioned large amount of Si mobilised (approximately 211000 ppm) in the case of the mineral acid experiment. This considerable attack on the silicates (largely quartz) present in the system by the more acidic fluids and such extremely high Si concentration indicate that the solution was highly effective at dissolving the matrix minerals. Such dissolution, leading to a reduction in solids volume and associated increase in porosity, could expose more surfaces of metal bearing minerals, and also increase permeability and enhance fluid flow through the system. However, a higher dissolved load could also cause more precipitation on cooling. This highlights the duality of such fluids, enhancing reservoirs through increased permeability, but potentially also leading to issues with precipitation in surface infrastructure.

Total concentrations of critical elements are approximately 50 ppb in the case of reaction with deionised water, 830 ppb in the case of reaction with acetic acid and 8500 ppb when mineral acid was used. There is a strong relation between acidity and the total amount of mobilised elements. In my dissertation, during batch experiments at higher temperatures, mineral acid was the best solvent, resulting in relatively high metal mobilisation and high concentration of Al and Si, which in practice would mean higher risk for scaling. Leaching with acetic acid resulted in moderate metal concentration and significantly lower Al and Si concentrations, suggesting this as a viable leaching option and a good compromise between useable metal release and scaling risk. Also, it could be more challenging to use mineral acids as leaching solvent in geothermal systems due to difficulties around transportation, handling, storage, and environmental issues. In terms of mobilised critical elements, acetic acid was more effective than deionised water but less so than mineral acid (both in terms of dissolved concentrations, and the spread of elements leached in detectable concentrations).

The results indicate however, that even a relatively mild leachant, such as acetic acid, with which the public is familiar as an everyday substance, can substantially increase leaching potential. In this case, a switch from deionised water to acetic acid generates a nearly 20-fold increase in dissolved load of the selected critical elements. Naturally, acetic acid may not be suitable for use under all circumstances; organic acids have a tendency to break down at elevated temperatures for example (though the natural breakdown of an injectant may be seen

as desirable in the long term), but these results highlight the potential of using such, relatively simple, fluids to enhance leaching in an EGS system.

**T4. I could successfully mobilise tungsten from solid samples with fluids under geothermal reservoir circumstances in a laboratory. I verified that it is possible to mobilise tungsten on an industrial scale with circulated fluid.**

The European Commission (2017) reviewed the necessary raw materials for the techno-economic development of the European Union and identified those materials that yielded a substantial supply risk (i.e. high uncertainties in securing sustainable supply) while also assessing current reserves and resources. Tungsten was evaluated as the leading element in terms of economic importance, with the supply risk above the determined threshold. Most of the tungsten is imported from China. To decrease the dependency on import (and to increase the efficiency of geothermal systems) I investigated if it is possible to mobilize tungsten from solid samples with fluids. In presented *in situ* experiments I artificially composed tungsten minerals with quartz. This included  $\text{CaWO}_4$  (the chemical analogue of scheelite) and  $\text{FeWO}_4$  (the chemical analogue of ferberite). I used deionised water, acetic acid (in 0,1 M concentration), mineral acid (in 0,13 M concentration) and sodium hydroxide (in 0,1 M concentration).

Tungsten leaching potential was investigated using a flow-through reactor with the characteristic physical properties of a geothermal reservoir. Tungsten minerals were tested at 200°C, 250°C and 300°C, and 0.5 and 1.0 mL/min flow rates to determine the most favourable conditions for the mobilisation of tungsten. In situ leaching yielded tungsten concentrations of 1,7 ppm in the leachates with pure ferberite and 182,9 ppm with pure scheelite. The 1:1 mixture of scheelite and ferberite resulted tungsten in the leachates in 32,5 ppm concentration.

Sodium hydroxide was the most effective in mobilising tungsten, resulting in 3074 ppm concentration (at 300°C temperature, 0,5 ml/min flow rate). If fluid with this tungsten concentration is produced from a reservoir at 1000 l/min flow rate, then 4,4 tonnes of tungsten is carried to the surface with the fluid. If the electroprecipitation metal extraction technology has 35% efficiency, then 1,5 tonnes of tungsten could be extracted daily. This is of course a theoretical potential, which is influenced by many parameters (i.e. the accessible amount of tungsten) and development of other technologies is also necessary.

**T5. I demonstrated that leaching tungsten with sodium hydroxide is much more efficient than leaching with acidic solutions at 200-300°C temperature range, in a flow-through system with short residence time. Under these circumstances the efficiency of tungsten leaching increases with temperature.**

As tungsten is rarely found in a pure form in the nature, in the laboratory experiments I mixed scheelite and ferberite in the ratio of 1:1. This mixture was then leached with different fluids, to study their leaching efficiency at different temperatures.

At 200°C temperature acetic acid mobilised 0,7 ppm tungsten at 0,5 ml/min flow rate in 180 minutes, 0,13 ppm at 1 ml/min flow rate in 90 minutes. The mineral acid could dissolve 7,46 ppm tungsten at 0,5 ml/min flow rate in 180 minutes, 0,23 ppm at 0 ml/min flow rate in 90 minutes. Sodium hydroxide was way more effective, mobilising 642,67 ppm tungsten at 0,5 ml/min flow rate and 479 ppm at 1 ml/min flow rate.

Reactions at 250°C temperature with acetic acid yielded 0,68 ppm tungsten at 0,5 ml/min flow rate and 0,4 ppm at 1 ml/min flow rate. Mineral acid could mobilise 0,37 ppm tungsten at 0,5 ml/min flow rate and 3 ppm at 1 ml/min. Leaching with sodium hydroxide resulted in 822,33 ppm tungsten at 0,5 ml/min flow rate and 757,33 ppm at 1 ml/min flow rate.

At the largest studied temperature, 300°C acetic acid could mobilise 0,76 ppm tungsten at 0,5 ml/min flow rate and 0,32 ppm at 1 ml/min. Mineral acid dissolved 0,17 ppm tungsten at 0,5 ml/min and 0,16 ppm at 1 ml/min. The most effective results were observed with the reaction of sodium hydroxide: 2488 ppm tungsten at 0,5 ml/min flow rate and 2090 ppm at 1 ml/min.

To dissolve and mobilise tungsten it is advised to use sodium hydroxide as opposed to acidic solvents, which proved 3-fold larger efficiency.

**T6. The potential electron transfer ensured by  $Fe^{2+}/Fe^{3+}$  had no facilitating effect on the amount and efficiency of metal leaching from solids.**

With geochemical modelling I had the opportunity to monitor parameters which were not measured during the experiments in laboratory. The equilibrium geochemical model showed that ferberite reacted with deionised water, acetic acid or mineral acid, in an oxygen rich environment, results in the formation of hematite. All of these solutions lead to hematite formation at every temperature tested, at every flow rate tested.

With sodium hydroxide ferberite shows remarkably larger reactivity than with deionised water or with acids. Due to this increased reactivity, a large amount of  $\text{Fe}^{2+}$  is present in the pore solution from the dissolved ferberite. Part of these  $\text{Fe}^{2+}$  ions are oxidized to  $\text{Fe}^{3+}$  due to the oxygen saturation of the input solution. However, the solution is ferberite is so intensive, that the oxygen content of the input solution is not sufficient to sustain oxidative conditions. This process results in magnetite formation due to the arisen reductive environment, which uses all available oxygen in the system. The formation of magnetite starts at the input side and lasts as long as there is ferberite.

The amount of iron in the solution is determined by the constant input solution. If there is not enough iron in the system, every metal is oxidized due the presence of oxygen. This results in  $\text{Fe}^{2+}$  losing an electron and forming  $\text{Fe}^{3+}$ . The solubility of  $\text{Fe}^{3+}$  is worse than  $\text{Fe}^{2+}$ , therefore  $\text{Fe}^{3+}$  precipitates from the solution. This would form iron oxides, the exact compound is controlled by the intensity of  $\text{Fe}^{2+}$  solution, which depends on the swiftness of ferberite solution.

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