Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

# Laboratory Investigations to Optimize Tungsten Mobilization Under Geothermal Reservoir Conditions

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**Keywords:** geothermal, EGS, tungsten, *in situ* leaching

## ABSTRACT

In a properly established engineered geothermal system (EGS) residence time and contact surface have crucial importance. In any scenario, during such utilizations of geothermal energy fluid injected into wells will react with the reservoir. Whether natural and artificial fractures are going to clog or propagate over time is mostly dependent on the characteristic of the reservoir. According to our hypothesis, tested in the EU H2020 project “CHPM2030”, an EGS system could be established in a way that fluid can react with, and dissolve nearby metal enrichments. Tungsten has long been identified as one of the most critical elements in terms of raw material accessibility in the EU, therefore the possibility of mobilizing tungsten from a geothermal reservoir was investigated in this study.

A custom-built flow-through reactor was used in our laboratory work to most precisely create the conditions of an EGS. There, scheelite and ferberite, the two most abundant tungsten minerals were crushed and reacted with different fluids with different physical parameters to obtain data about tungsten mobilization under geothermal reservoir conditions. In this research, deionized water, acetic acid, sodium hydroxide, and the mixture of hydrochloric acid and nitric acid were tested as possible leaching agents. All reactions were conducted at around 250 bars pressure, which corresponds to the pressure of the hypothesized EGS. The reactor was heated up to 200°C, 250°C and 300°C temperature while 0.5 ml/min – 1.0 ml/min flowrates were maintained by a HPLC pump. At the exit of the reactor a slow but continuous flow could be observed, and samples collected. The leachate samples were analyzed with single element ICP-OES.

Concentration of leaching agents were kept relatively low (around 0.1 M), to maintain possible future applicability by limiting the potential environmental and social impact of pilot scale implementations. *In situ* leaching yielded tungsten concentrations of 1–3074 mg/L in the leachates, with sodium hydroxide being the most effective in mobilizing tungsten from the mixture of ferberite and scheelite.

## 1. INTRODUCTION

The idea of further harnessing brines has received considerable attention in enhancing the economics of geothermal energy utilization, with lithium being the first element to be extracted from geothermal fluids. These lithium-producing operations have taken place in felsic magmatic environments in New Zealand (Kennedy, 1961; Mroczek et al., 2015) and various igneous sources, including granitoid environments, in the United States (Bourcier et al., 2005; Kesler et al., 2012; Neupane & Wendt, 2017). Such geological settings are optimal for establishing an EGS, with the co-production of metals alongside energy production presenting a feasible option in many cases (Németh et al., 2016; Kilpatrick et al., 2017; Szanyi et al., 2017). The proven viability of lithium production from geothermal brines serves as a good motivation to investigate the production potential of extracting other elements.

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. 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. It is essential for many high-strength, high-temperature applications, such as wood and metalworking, mining, steel hand tools, wear protection, ammunition, studded tires and chemical use (Amer, 2000; Luo et al., 2003; Bednar et al., 2008). It has also been designated as a ‘critical material’ and ‘strategic resource’ within the European Union (Linnen et al., 2012; EC, 2017).

Tungsten is commonly found as a mobile tungstate anion in the environment, which is able to create polymers with itself and other anions (Bednar et al., 2008). It is utilized from ore (0.3%–1% WO3), ore concentrate (7%–60% WO3) and scrap (40%–95% WO3) and potentially via unconventional production, such as geothermal brines (Onozaki et al., 1976; Luo et al., 2003). Che et al. (2013) identified tungsten concentration ranges from 12 mg/L to much higher values in its natural (granitoid or pegmatiod) environments. They also found that rocks with high tungsten concentrations are often very rich in lithium as well. Therefore, ongoing lithium extraction from such environments provides a potential analogue for targeting tungsten production from similar environments.

## 2. EXPERIMENTAL

### 2.1 High-pressure, high-temperature flow-through reactor setup

The leaching processes were investigated under continuous flow conditions using a flow-through reactor (Figure 1). The reaction took place in a stainless steel high-performance liquid chromatography (HPLC) column that was 250 mm in length, with an inner diameter of 25.4 mm. The pressure in the column was maintained using an Ecom Kappa 10 Single-Plunger HPLC pump (Czech

Republic). A 50-cm stainless steel capillary and a fluid back-pressure regulator were fitted at the outflow of the column. The length of this tubing was determined in order to cool the outflowing fluid below 90°C before being depressurized. Heating bands were attached to the column and controlled using a thermostat (WH-1435D proportional–integral–derivative controller digital thermostat with ±1°C control regulation). This externally heated pressure vessel (EHPV) was loaded with an approximately 126 $cm^3$ sample and operated at a range of temperatures (200°C, 250°C and 300°C) and a pressure of approximately 250 bar. These parameters correspond to depths of around 2.5–3 km in an average geothermal field (MIT, 2006; Breede et al., 2013). Two different flow rates (0.5 and 1.0 mL/min) were used in the reactor during the experiments, which resulted in a contact time of 30–100 min between the fluid and rock, allowing sufficient sample volumes to be collected for the chemical analyses.

**Figure 1: Flow-through EHPV (left) and temperature control panel (upper right) of the HPLC pump (lower right) used in laboratory experiments**

## 3. RESULTS AND DISCUSSION

### 3.1 In situ leaching of scheelite with DI water eluent

The initial experiments were designed with pure tungsten minerals (scheelite or ferberite) and finally with a 1:1 mixture of scheelite and ferberite to isolate the effect of each mineral. The reactor was first filled with 8.0 g of scheelite (chemical grade) and inert quartz sand, which corresponds to a 5% concentration of the 'active' material in the initial solid sample. Tungsten content of the solid $CaWO_4$ sample was 343 mg/kg. Corresponding ICP-OES results from the scheelite leachates are shown in Figure 2.

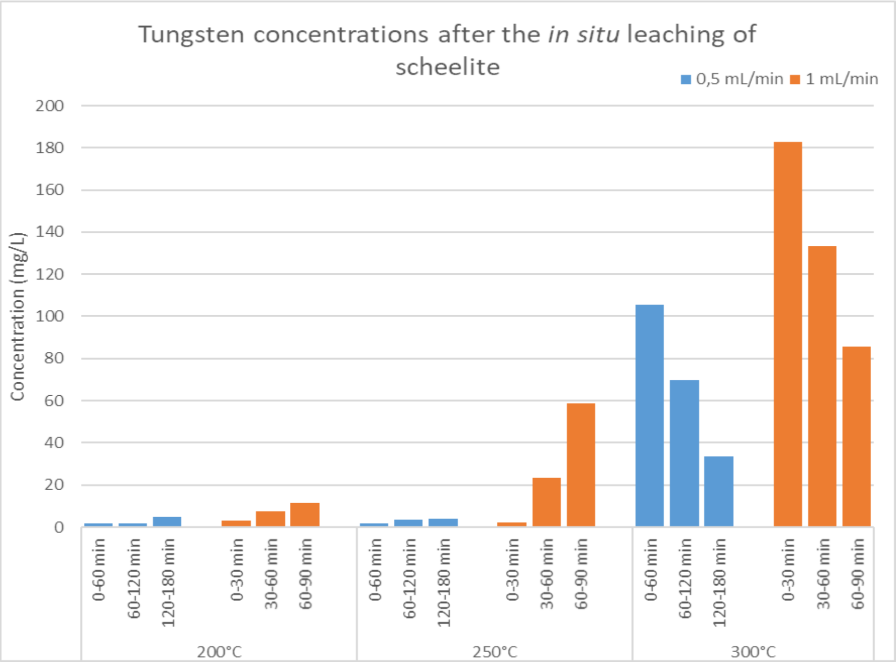

**Figure 2: Tungsten concentrations in the leachate after contacting scheelite with DI water under different geothermal reservoir scenarios**

The main trend observed in the *in situ* leaching of scheelite is the temperature effect, with increased tungsten release occurring as the temperature increased. The maximum concentrations at 200°C were 5 and 11 mg/L at 0.5 and 0.1 mL/min flow rates, respectively. The 0.5 mL/min flow rate yielded approximately 4 mg/L, and the 1.0 mL/min flow rate yielded 60 mg/L at 250°C. The concentration of the released tungsten increased with time, with the concentration at 250°C and 1 mL/min increasing from 2 mg/L at 30 min to 60 mg/L at 90 min. The best results were observed at 300°C, ranging from 35 to 180 mg/L. However, it is important to note that tungsten concentration in the leachates decreased over time at this temperature. The reason for this decreasing trend could be that the mobility of scheelite is highest at 300°C among the investigated temperatures, with the access to fresh fluid being the rate-limiting step in tungsten release. As soon as the fresh DI water contacted the ‘active’ material, it could rapidly dissolve as many ions as it could carry, such that its mobilization rate declined over time.

### 3.2 In situ leaching of ferberite with DI water eluent

Given that both $Fe^{2+}$ and $Fe^{3+}$ ions are commonly found in natural environments, ferberite is chosen to determine if potential electron transfers would enhance tungsten mobilization. The reactor was filled with 8.0 g of ferberite (concentrate from a tungsten mine) and inert quartz sand, which corresponds to a 5% concentration of the ‘active’ material in the initial solid sample. Tungsten content of the solid $FeWO_4$ sample was 773 mg/kg. Corresponding ICP-OES results from the ferberite leachates are shown in Figure 3.

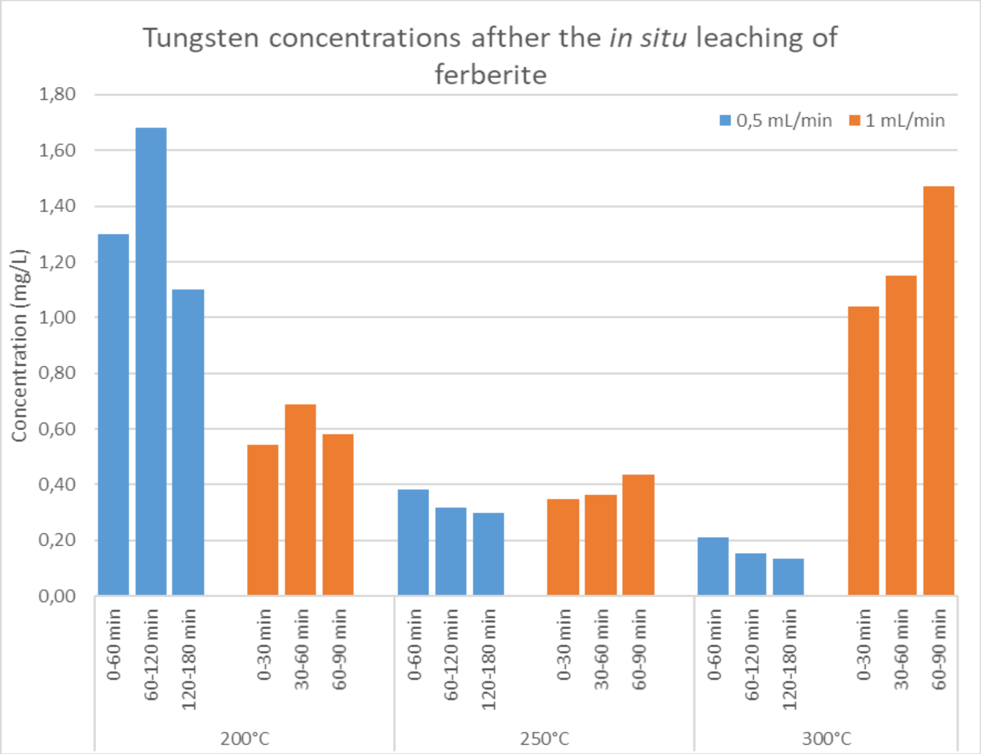

**Figure 3: Tungsten concentrations in the leachate after contacting ferberite with DI water under different geothermal reservoir scenarios**

There is no distinct trend in the leaching of ferberite among the different geothermal reservoir scenarios, with *in situ* leaching yielding concentrations between 0.1 and 1.5 mg/L. The highest concentrations were reached at 200°C and a 0.5 mL/min flow rate (>1 mg/L), whereas mobilization was ineffective for the same flow rate at 250°C (0.3–0.4 mg/l) and 300°C (0.1–0.2 mg/L). Mobilization was more effective at these temperatures and a 1.0 mL/min flow rate, yielding 0.3–0.5 mg/L concentrations at 250°C and >1 mg/L concentrations at 300°C. The difference between the highest and lowest concentrations in each scenario was negligible, and neither the temperatures nor the flow rates exhibited a notable influence on the mobility of ferberite, such that the leaching could be considered constant (low) throughout the experiments.

### 3.3 In situ leaching of the 1:1 ratio mixture of scheelite and ferberite with DI water eluent

A relatively mobile mineral, scheelite, was mixed with an immobile mineral, ferberite, which could potentially increase the rate of leaching by providing a $Fe^{2+}/Fe^{3+}$ buffer. The reactor was filled with 4.0 g of scheelite, 4.0 g of ferberite and inert quartz sand, which corresponds to a 5% concentration of the ‘active’ material in the initial solid sample. Tungsten content of the solid mixture sample was 337 mg/kg. Corresponding ICP-OES results from the conducted experiments are plotted on Figure 4.

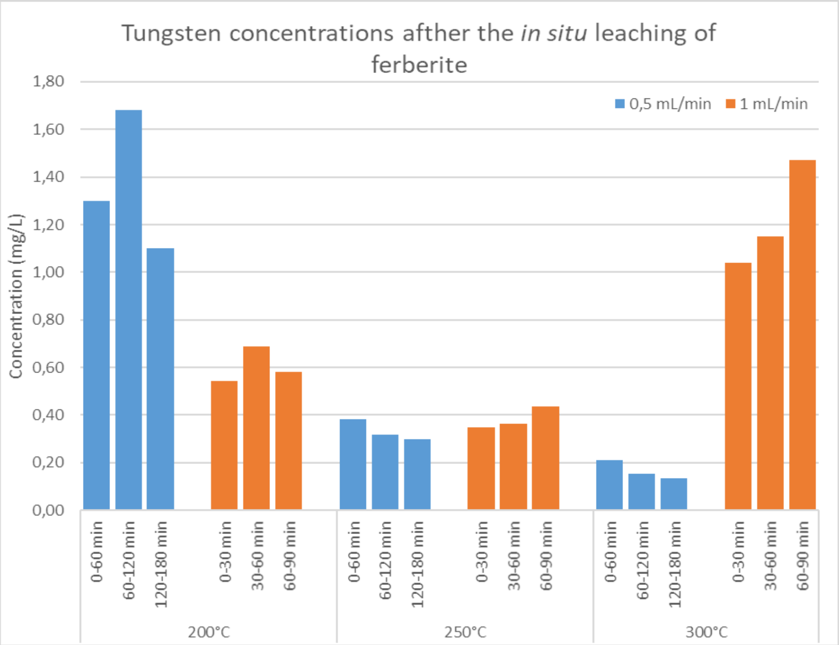

**Figure 4: Tungsten concentrations in the leachate after contacting the scheelite–ferberite mixture with DI water under different geothermal reservoir scenarios**

The mixture of relatively mobile (scheelite) and immobile (ferberite) tungsten minerals yielded minimum and maximum concentrations of 0.7 and 32.5 mg/L among the different geothermal reservoir scenarios. This concentration range was lower than that of the pure scheelite experiments and higher than that of the pure ferberite experiments. The higher flow rate could enhance the mobilization as the tungsten concentrations increased from 8 to 26 mg/L at 250°C and from 15 to 32 mg/L at 300°C when the flow rate increased from 0.5 to 1.0 mL/min, respectively. This indicates that the rate-limiting step in the experiments is still the solubility of scheelite, with most of the accessible scheelite molecules being rapidly mobilized by DI water, whereas the ferberite molecules remain immobile and do not facilitate tungsten release, therefore leading to lower tungsten concentrations in the mixtures.

### 3.4 In situ leaching of the 1:1 ratio mixture of scheelite and ferberite with acetic acid eluent

After experiencing the behavior of scheelite and ferberite with DI water, it is interesting to see if different environmentally acceptable acids could improve the efficiency of tungsten leaching. A relatively benign fluid, acetic acid with the concentration of 0.1 M was used. The reactor was filled with 4.0 g of scheelite, 4.0 g of ferberite and inert quartz sand, which corresponds to a 5% concentration of the 'active' material in the initial solid sample. Tungsten content of the solid mixture sample was 337 mg/kg. Corresponding ICP-OES results from the conducted experiments are plotted on Figure 5.

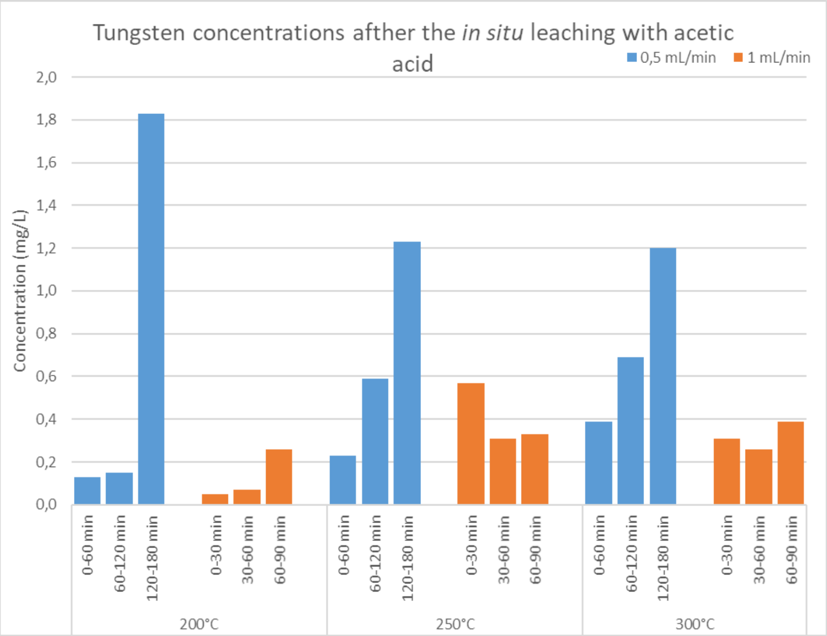

**Figure 5: Tungsten concentrations in the leachate after contacting the scheelite–ferberite mixture with acetic acid under different geothermal reservoir scenarios**

After leaching with acetic acid, tungsten concentration ranges between 0 and 2 mg/mL. Compared to previous experiments these concentrations are very small, leaching was inefficient. Trends of solution indicate that the longer experiment resulted in better mobilization, but considering the absolute value of mobilized tungsten, this trend is irrelevant.

### 3.5 In situ leaching of the 1:1 ratio mixture of scheelite and ferberite with mineral acid eluent

After exploring leaching efficiency with DI water and acetic acid, it is interesting to see if the leaching with acetic acid was ineffective based on chemical reactions (coagulation or the formation of insoluble substances) or physical parameters (temperature, pressure, flow rate or pH) had negative effect on the leaching, therefore a different acid was also tested. The efficiency of a mineral acid with the concentration of 0.1 M was explored, which was composed of 3:1 $HNO_3$ and HCl. The reactor was filled with 4.0 g of scheelite, 4.0 g of ferberite and inert quartz sand, which corresponds to a 5% concentration of the 'active' material in the initial solid sample. Tungsten content of the solid mixture sample was 337 mg/kg. Corresponding ICP-OES results from the conducted experiments are plotted on Figure 6.

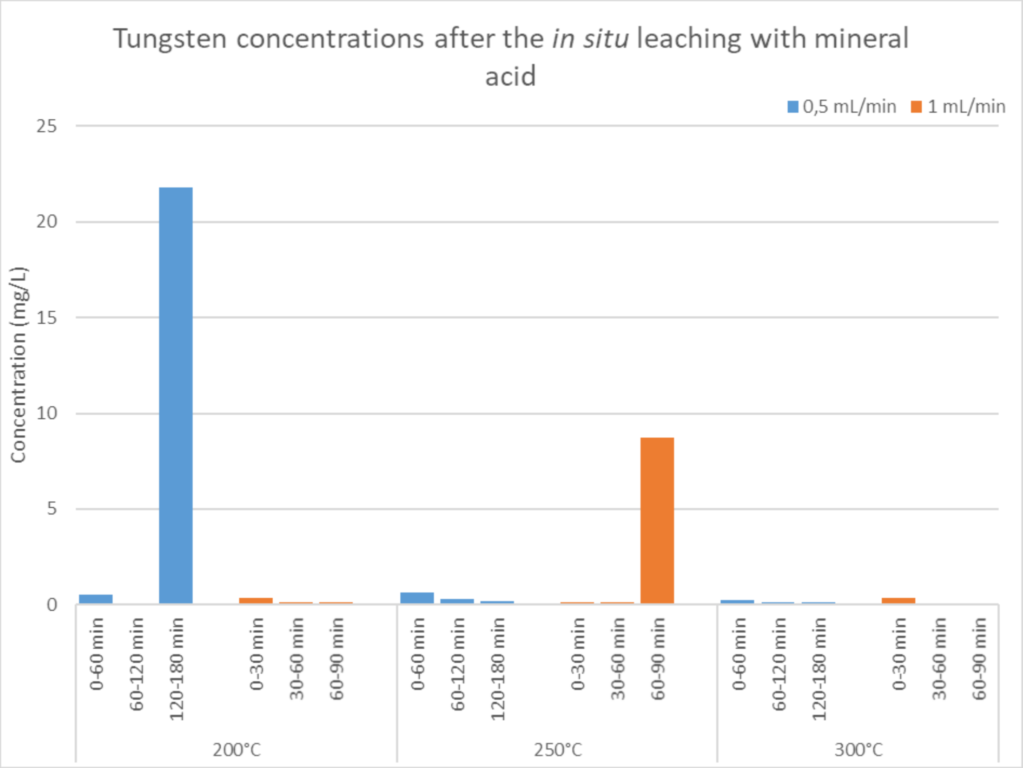

**Figure 6: Tungsten concentrations in the leachate after contacting the scheelite–ferberite mixture with mineral acid under different geothermal reservoir scenarios**

Leaching of tungsten minerals with mineral acid resulted in 0 – 22 mg/mL concentration in the leachates, indicating better effectiveness than leaching with acetic acid. Concentration are still low, and trends were not observed.

### 3.6 In situ leaching of the 1:1 ratio mixture of scheelite and ferberite with sodium hydroxide eluent

Experiencing trends with DI water and with different acids, the leaching efficiency of a basic fluid was also explored, this section describes leaching conducted with sodium hydroxide with the concentration of 0.1 M was used. The reactor was filled with 4.0 g of scheelite, 4.0 g of ferberite and inert quartz sand, which corresponds to a 5% concentration of the 'active' material in the initial solid sample. Tungsten content of the solid mixture sample was 337 mg/kg. Corresponding ICP-OES results from the conducted experiments are plotted on Figure 7.

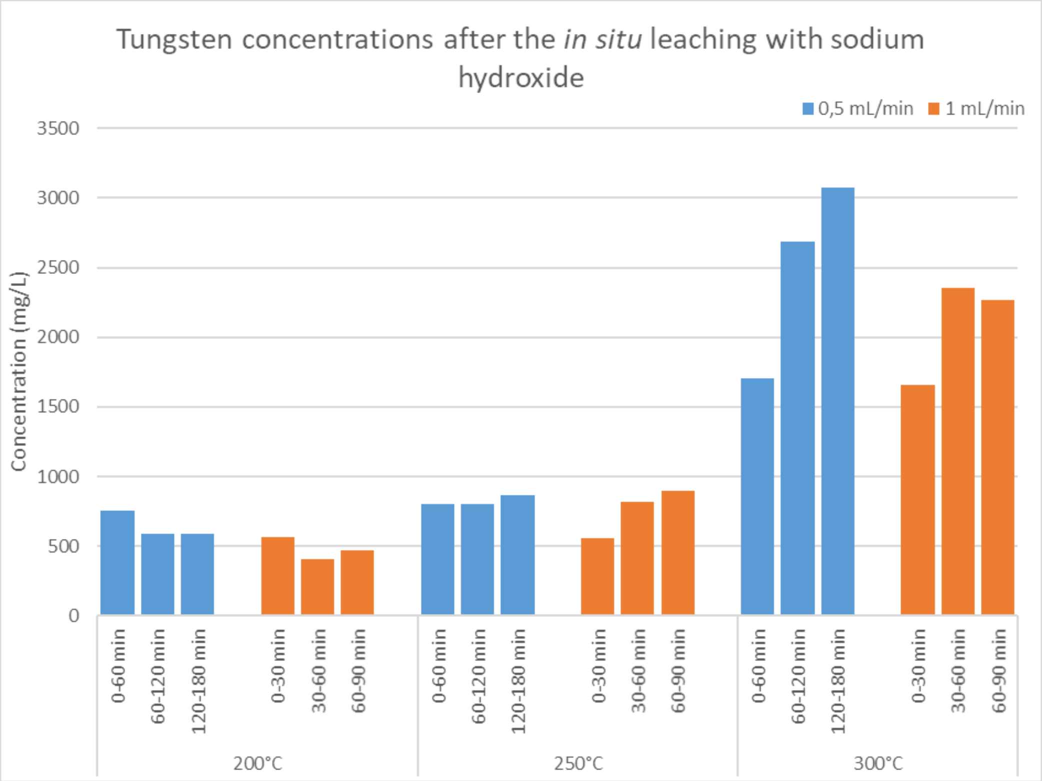

**Figure 7: Tungsten concentrations in the leachate after contacting the scheelite–ferberite mixture with sodium hydroxide under different geothermal reservoir scenarios**

Leaching with sodium hydroxide resulted in the most promising concentration throughout the experiments. Tungsten concentration in the leachates ranges from 409 mg/mL to 3075 mg/mL, which indicates notable mobilization rates. The effect of temperature influences most the leaching of tungsten minerals: at 200°C temperature concentrations are below and a little bit above 500 mg/mL, at 250°C temperature 500 – 1000 mg/mL concentration of tungsten was mobilized and at 300°C concentrations were more than 1500 mg/mL, leaching with 0.5 ml/min exceeded 3000 mg/mL concentration.

## 4. CONCLUSIONS

Here, a continuous flow-through EHPV was used to study fluid–rock interactions under various geothermal reservoir conditions and investigate the potential of tungsten leaching and mobilization in an EGS. Different tungsten minerals (scheelite and ferberite) were contacted with DI water, acetic- and mineral acid and sodium hydroxide at 200°C, 250°C and 300°C under 250–280 bar pressure and different flow rates. Scheelite was much more mobile under the tested experimental conditions than ferberite, the effect of different fluids was tested on the 1:1 mixture of these minerals. The experiments at higher temperatures yielded the highest tungsten concentrations, of up to 3000 mg/L in the leachate from reaction with sodium hydroxide. Concentrations of only 1–22 mg/L were obtained in the leachate from reaction with acids.

The effects of different physical parameters that could influence mild leaching were tested and compared, with the leaching time and temperature yielding significant differences in the tungsten concentrations during the leaching experiments. However, we noted that the influence of pressure on tungsten mobilization could not be analytically investigated with the current experimental setup because of the pressure fluctuation in the single-plunger pump within a given time interval. This resulted in minor pressure differences during each experiment, but the pressure ranges were still representative of the observed pressures in geothermal reservoirs. These pressure fluctuations did not influence leaching above a certain pressure such that the observed time and temperature differences during leaching yielded representative and realistic concentrations for the tested tungsten minerals.

Time is an important parameter during the in situ leaching of tungsten. Although it seems intuitive that a longer leaching time would result in a higher mobilization rate, this is not always the case. The dissolution of tungsten from pure scheelite reached equilibrium rapidly (usually in the first 30 min), with the longer experiments yielding lower concentrations over time. This trend becomes more obvious at higher temperatures, and the experiments at lower temperatures yielded low concentrations, regardless of leaching time. Nevertheless, pure scheelite yielded the highest concentrations compared to pure ferberite and scheelite–ferberite (1:1) mixture. Pure ferberite exhibited a much different trend, as it was much harder to mobilize, and the concentrations were much lower. Although the mobilization rate was lower in the first hour of the flow-through leaching compared to that in the second hour, the increase in mobilized material was only a few mg/L. The scheelite trend was more dominant in the experiments with the scheelite–ferberite (1:1) mixture, but ferberite was still difficult to mobilize in the mixture.

These experiments indicate that temperature has the largest influence on the in situ leaching of tungsten. The higher temperature (300°C) experiments resulted in much more effective dissolution and mobilization than the lower temperature (200°C) experiments.

Higher temperatures were not considered as the currently used 200°C–300°C temperature range represents the vast majority of high-enthalpy geothermal reservoirs.

The influence of the solid particle grain size on leaching was not investigated, with a uniform grain size used in the experiments for a better comparison among the experiments. This grain size, which was based on previous studies, was chosen to speed up the reaction time by increasing the contact surface for fluid–rock reactions. We note that this may not represent the actual contact surface, -volume or -time of a geothermal reservoir so that future studies should explore the effect of grain size on tungsten mobilization. Future studies should also investigate the effect of different leaching fluids in the flow-through reactor under the same physical properties and experimental conditions, as well as different tungsten mineral compositions, to further constrain those parameters that effect tungsten mobilization in geothermal settings.

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