

# Tungsten speciation and its geochemical behavior in geothermal water: A review

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**Abstract.** Tungsten and most of its compounds remain one of the least regulated substances. As the potential toxicity of tungsten has been reported, the stereotypes about tungsten are gradually being broken. Areas with intense magmatic hydrothermal activity are likely threatened by geothermal tungsten (up to 1037 µg/L of tungsten was detected in the geothermal waters from a magmatic hydrothermal system in Tibet, Daggyai), and the geothermal developers should be cautious during the utilization of geothermal resource. This paper reviews the studies on transformation of aqueous tungsten species, distribution of tungsten in geothermal waters, and critical geochemical processes (or parameters) controlling geothermal tungsten concentrations. The mobility of aqueous tungsten depends on environmental pH, its complexation with sulfide, and its sorption onto Fe(III) oxides/oxyhydroxides. More attention still needs to be paid to environmental geochemistry of tungsten, in view that there are limited literatures reporting the thermodynamic properties of tungsten compounds at high temperatures and the models delineating the geochemical behavior of tungsten.

## 1 Introduction

Tungsten is a transition metal found in Group VI of the Periodic Table of elements, and was considered as an environmentally benign element from a historical view. However, the childhood leukemia cluster afflicting Nevada, along with two analogous toxicological profiles appeared in Arizona and California (USA), stimulated tungsten-related studies that the environmental exposure to elevated tungsten concentrations may be responsible for these childhood leukemia clusters. Indeed, animal studies in laboratory have shown that tungsten can be toxic and may be carcinogenic [1-3].

Of the various sources of tungsten in the environment, the geothermal fluids are often enriched in tungsten and geothermal activities make its fate and transport more complicated. Compared with other hazardous constituents in geothermal water, the rules of tungsten mobilization and transformation are ambiguous, which should be paid more attention to during the utilization of geothermal resources. This review attempts to summarize the existing literature on the occurrence and environmental behavior and estimate the factors controlling tungsten concentrations in geothermal water.

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## 2 Aqueous tungsten speciation

Tungsten (W) and its compounds have traditionally been regarded as substances of limited aquatic solubility and mobility. However, it has been reported [4] that metallic tungsten possesses a slow corrosion rate of  $3.8 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  with distilled water at  $38^\circ\text{C}$ , resulting in an equilibrium tungstate concentration of  $10^{-3}$  M in solution. Tungsten speciation in aqueous solution becomes complicated and is not completely understood.

Oxyanion polymerization of W depends strongly on pH, as the reaction occurs upon acidification and the formation of kinetic intermediate [4]. The monomeric state of tungstate is only stable under alkaline conditions ( $\text{pH}>10$ , which is debateable and the accepted pH value in the range 7 to 10) in solutions free of complexation agents. While at very low pH ( $\approx 1$ ), W precipitates as tungsten oxide ( $\text{WO}_3\cdot\text{H}_2\text{O}$ ). In between these upper and lower pH bounds, monomeric tungstate tends to form different polyoxoanions. Many isopolytungstates are not very stable in solution and exist only in short-lived forms (at scales of minutes and hours); however, at much longer time scales (weeks) stable polytungstates generate, such as meta- and para-tungstates. The speciation equilibrium of sodium metatungstate ( $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$ ) in the pH range 4.5 to 10 was studied using NMR spectroscopy [6]. Metatungstate was found to decompose to paratungstate A ( $\text{W}_7\text{O}_{24}^{6-}$ ) with the addition of base, which slowly converted to paratungstate B ( $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ ). The kinetics of equilibrium may take 8 months to stabilize. The environmental implications of these transformations are not addressed. However, from the available literature and experimental studies, it appears that monomeric tungstate ( $\text{WO}_4^{2-}$ ) is the principal soluble species in alkaline environments, whereas numerous possibilities for polymerized forms prevail at acidic environments.

The situation becomes extremely complicated in the presence of complexing ions or ligands. For example, with halides, W(VI) forms the octahedral complexes -  $\text{WX}_6^-$  (where  $\text{X} = \text{F}, \text{Cl}$  and  $\text{Br}$ ) and  $\text{WF}_8^{3-}$ . Under anoxic and sulfidic conditions, the presence of dissolved sulfide reacts with tungstate to form thioanions ( $\text{WO}_{4-x}\text{S}_x^{2-}$ ,  $x = 1-4$ ) [7, 8]. In addition, many heteropolytungstates with different structures (Keggin, Dawson or Finke type), obtained from various conditions, may be also soluble in aqueous systems. Among them, Keggin-type heteropolytungstates are much more stable than isopolytungstates over a wide range of pH values and water temperatures [5]. They can be considered as the metatungstate ion, where the central hydrogen atoms are replaced by other cations. Several well-known anions of Keggin structure are  $\text{PW}_{12}\text{O}_{40}^{3-}$ ,  $\text{SiW}_{12}\text{O}_{40}^{4-}$ ,  $\text{ZnW}_{12}\text{O}_{40}^{6-}$  and  $\text{AlW}_{12}\text{O}_{40}^{5-}$ . Chemical conditions of geothermal waters may be quite similar to the conditions under which thermal synthesis is conducted in the laboratory. For instance, the synthesis of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  involve only heating of a mixture of constituents under acidic conditions, in particular  $\text{WO}_4^{2-}$  and  $\text{HPO}_4^{2-}$ . Therefore, it was suggested that tungsten in geothermal waters presents in the form of heteropolytungstates.

Although advances in analytical techniques may offset some of the complexities [7, 9-11], aqueous tungsten speciation is still worthy of further study with respect to the severely limited information about its chemical and thermodynamic properties.

## 3 Abundance and distribution in geothermal waters

Background values of W in natural waters are in trace amounts unless W is deposited or influenced by anthropogenic activities. In addition, the areas of intense geothermal activities may be another cause for tungsten enrichment. Studies of hydrothermal geochemistry of W lend considerable support to the suggestion that geothermal fluids may readily transport tungsten at concentrations of thousands of ppm at temperatures ranging from  $200$  to  $600^\circ\text{C}$  [12]. Therefore, the contents of W in geothermal waters with the

existence of a deep parent geothermal liquid elevate significantly. Whereas, for the geothermal systems with non-magmatic sources, W may also be enriched in geothermal waters as a result of the strong influence of water-rock interactions. A summary of limited occurrence data for W in geothermal waters is recorded in Table 1.

**Table 1.** Tungsten abundance in geothermal waters.

Location	Concentration ( $\mu\text{g/L}$ )	Reference
<i>Surface geothermal waters, Iceland</i>		
NaCl-type waters	2.4 to 88	[13]
Steam-heated acid-sulphate waters	0.01 to 6.9	[13]
Hot spring in southeastern Carson Desert, USA	58.5	[14]
<i>Hot springs in South Nahanni River area, Canada</i>		
Nahanni Headwater	224.5	[15]
East Cantung	121	[15]
West Cantung	59.6	[15]
Hot spring in geothermal system of Daggyai, Tibet, China	1037	This study

It has been noted that three hot springs in South Nahanni River area (Canada) contained more than 50  $\mu\text{g/L}$  tungsten, and the highest concentration was up to 224.5  $\mu\text{g/L}$  [15]. These are alkaline hot springs adjacent to or in Cretaceous granites (containing numerous wolframite, a W ore). Seiler et al. [14] detected the tungsten concentration of 58.5  $\mu\text{g/L}$  from the hot spring in southeastern Carson Desert of Nevada (USA) and most wells in the Fallon area, near Carson Desert, with W concentrations greater than 50  $\mu\text{g/L}$  are associated with geothermal sources. There are three geothermal areas (near Stillwater, Navy Air State, and between Big Soda Lake and Upsal Hogback) beneath the Carson Desert. Geothermal water flows upward from depths greater than 2400 m where it mixes with cold water in shallow, intermediate and deep aquifers, which is one of the vital processes that control W concentrations in groundwaters from the Carson Desert. Kaasalainen and Stefansson [13] categorized the surface geothermal waters in Iceland into three groups based on their chemical composition, namely NaCl waters, steam-heated acid-sulfate waters and mixed waters. NaCl waters with  $\text{pH} > 8$  are considered to represent geothermal fluids that have undergone boiling in the upflow. The elevated W concentrations of this type of geothermal waters in Iceland ranged from 2.4 to 88  $\mu\text{g/L}$ . Steam-heated acid-sulfate waters typically had a  $\text{pH} < 4$ , indicating that they form by condensation and mixing of steam in shallow non-thermal waters. And the W concentration reduced to  $<0.01$  to 6.9  $\mu\text{g/L}$  under the acidic pH values. In our studies, up to 1037  $\mu\text{g/L}$  of tungsten was detected in the geothermal waters from a magmatic hydrothermal system of Daggyai in Tibet (China), which was collected in August 2018 and has not yet been reported.

## 4 Mineral-water interactions

### 4.1 Controls on tungsten mobilization

The reactions of W with water play a major role in its behavior and mobility. As mentioned before, W can form a large variety of oxyanions and complexing anions. The speciation of W may affect its mobilization due to dynamical instability of many isopolytungstates. The

advanced potential-pH equilibrium diagrams - the 3D Pourbaix diagrams relating the reduction potential, pH and concentration of different tungsten-based compounds have been constructed by Nave and Kornev [16]. These diagrams clearly indicate the complexity of chemical behavior of tungsten in aqueous solutions. But there is a tendency to dissolve  $\text{WO}_4^{2-}$  under alkaline conditions.

Rock leaching is important in all-type waters and favourable physical and geochemical conditions in aquifers may promote tungsten mobilization and accumulation. This is in agreement with previous work suggesting tungsten to be mobile at temperatures below 150 °C [17]. Although the primary minerals of tungsten, scheelite ( $\text{CaWO}_4$ ) and wolframite [ $(\text{Fe}, \text{Mn})\text{WO}_4$ ], are only slightly soluble, the degree of mobility of W (mainly as  $\text{WO}_4^{2-}$ ) is probably high under neutral or alkaline conditions.

W has a high affinity with sulfide in groundwater. The predicted geochemical behavior of W relies to a large extent on the results of the aqueous speciation calculations. However, some uncertainty remains in the stoichiometry and stability of thio- and mixed oxy-thio species at high temperatures. Recent studies [7, 8] suggest that W speciation may be important in geothermal waters containing reduced S species and thus their behavior may not be optimally simulated by the geochemical modelling. Despite these uncertainties, it can be concluded that progressive water-rock interaction may eventually result in W removal into secondary minerals including sulfides. The mobilization of W is also influenced by pH-controlled adsorption. Seiler et al. [14] observed that all samples with W concentrations greater than 50  $\mu\text{g/L}$  have pH values greater than 8.0 and geochemical modelling indicates that tungsten in these samples exhibits less than 10 % adsorption.

Microbial activities also affect the tungsten mobility in solution. The Fe- and Mn-oxidizing bacteria can significantly facilitate the breakdown of W containing minerals such as wolframite and release soluble tungsten compounds [18]. These bacteria oxidize Fe and Mn, which destroy the crystalline structure of wolframite, and further release of W soluble compounds may occur.

## 4.2 The role of iron oxides

Generally, elevated arsenic concentrations in groundwater may have elevated W concentrations. Recent studies have confirmed that the similar geochemical behavior between W and As also reflect in the strong sorption to Fe(III) oxides/oxyhydroxides at acidic to circumneutral pH via sorption experiments and modelling. A 2-pK Diffuse Layer Model and a 1-pK CD-MUSIC model was used by [19] to describe tungstate sorption on ferrihydrite at acidic pHs. Kashiwabara et al. [20] found that W shows a much larger adsorption on ferrihydrite than Mo. Sun and Bostick [21] examined that aqueous W speciation is of critical importance for regulating W adsorption on ferrihydrite. It is suggested that polyoxytungstates and heteropolytungstates adsorb to a lesser degree than tungstate onto ferrihydrite and presumably other minerals. Cui and Johannesson [22] concluded that tungstate adsorption onto pyrite increased with decreasing pH. Rakshit et al. [23] adopted an in situ ATR-FTIR probe to determine the sorption mechanism of W on hematite at fixed pH values ranged from 4.6 to 8.1. Xu et al. [24] found that tungstate exhibits stronger competitive adsorption on goethite than molybdate.

In addition, W may release to solution via reductive dissolution of W-sorbed Fe oxyhydroxides through oxidation of organic C. This mechanism is proposed by Smedley and Kinniburgh [25] as one of the principal causes of high As concentrations in ground water. Although the evidence for reductive dissolution of Fe and Mn hydroxides releasing W to groundwater is not conclusive, W concentrations in groundwater are basically consistent with adsorption as a control.

## 5 Conclusion

In this review, W and its compounds are no longer regarded as environmentally inert substances. The monomeric tungstate is stable in solution at alkaline pH, while its polymeric species prevail at acidic and neutral environments. In the presence of complexing ligands, the system becomes much more complicated as a large number of soluble complexing anions or heteropolytungstates may develop under the specific conditions. In terms of W sources, geothermal activity is a noticeable process in aqueous environment. Either magmatic activity or strong water-rock interaction makes geothermal water become enriched with high concentrations of W. The factors controlling W concentrations in natural waters include environmental pH, its complexation with sulfide, and its sorption onto Fe(III) oxides/oxyhydroxides.

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