

Characterization of tungsten distribution in tungsten-rich slag and sediment by leaching experiment

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Abstract

The adverse environmental effects of tungsten have been underestimated for a long time. Recent studies have demonstrated that dissolved tungstate is mobile in aqueous environments and exhibits severe toxicological impacts. If substantial tungsten slags were directly exposed, they would potentially pollute the surrounding waters and soils. The objective of this study was to investigate the pollution and ecological risks of tungsten-rich slags and sediments as a result of leaching. In this study, samples of tungsten-rich slags and sediments were collected from Chenzhou and Tengchong (China), with the highest tungsten concentration up to 378.1 mg/kg. To investigate the pollution and ecological risks of tungsten-rich slags and sediments as a result of leaching, sequential extraction procedures (SEP) and batch leaching experiments were conducted. According to the Tessier SEP results, the residual fraction accounted for more than 90% of the total tungsten in most samples, while the Wenzel SEP results showed over 52% of the hydrous oxides bound fraction except for the samples SP02 and ZN02. Thus, the Tessier SEP underestimated the proportions of the Fe and Al oxides bound fraction and the environmental risks of tungsten. In contrast, the Wenzel SEP was superior to the Tessier SEP in terms of extracting the amorphous hydrous oxides bound fraction and crystalline hydrous oxides bound fraction of tungsten due to the use of more suitable extraction reagents. The leaching experiments demonstrated the tungsten concentrations in the leachate samples were up to 105.6 µg/L. Notably, leaching of tungsten from the tungsten-rich slags and sediments under acid conditions was less effective than under alkaline conditions, which was attributed to the strong adsorption of tungsten onto Fe/Al (hydro)oxides under acid conditions.

1. Introduction

Tungsten, a transition metal element of Group VI in the Periodic Table of elements, occurs as a trace element in natural waters (Koutsospyros et al., 2006). Due to the nontoxicity of tungsten in the form of metal or alloy and its weak migration in the environment, its environmental impacts have not attracted enough attention for a long time. However, over the last decade, it has been demonstrated that the solubility and possible leaching of tungsten is higher than previously determined (Dermatas et al., 2004; Bednar et al., 2009; Sen Tuna and Braida, 2014). Tungsten, in the natural waters and sediments, occurs predominantly as monomeric tungsten oxyanion WO_4^{2-} (where tungsten is in its highest oxidation state, + 6) (Kletzin and Adams, 1996). Furthermore, recent studies showed that mono-tungstate was mobile in aquatic systems and exhibited severe ecotoxicological impacts (Seiler et al., 2005; Bednar et al., 2009; Clausen and Korte, 2009; Tuna et al., 2012; Johannesson et al., 2013). For example, the environmental geochemical investigation indicated that the abnormal concentration of tungstate in the environment may be closely related to the outbreak of leukemia in young children (Sheppard et al., 2007; Steinberg et al., 2007). In addition, clinical studies have shown that high levels of tungstate in people's urine or blood can trigger seizures, strokes or cardiovascular disease (Marquet et al., 1996; Tyrrell et al., 2013). In view of the above, tungsten is newly regarded as an arisen environmental pollutant by the United States Environmental Protection Agency (EPA, 2008).

China possesses the maximum tungsten resources (**1,900,000 metric tons**) in the world, which is also been the world's central tungsten consumer and exporter (USGS, 2018). However, overexploitation and outdated technology in past decades produced a large amount of tungsten slags (Liu et al., 2010). Notably, the cumulative amount of tungsten slag in China reached 1 million tons, what is worse, more than 70 thousand tons of tungsten slag were produced annually (Li et al., 2019a). Due to lack of proper management measures and economic commercial disposal, substantial amounts of tungsten slags were directly exposed to the land surface, or remained uncovered in massive piles, releasing tungsten into the environment by certain geochemical processes, thus contaminating the underground waters and surrounding soils.

For example, tungsten, in soils of Zakamensk known as one of the biggest ore mining centers in the former Soviet Union, was 42–55 times higher than the background area, and the concentrations of heavy metal in the investigated area significantly exceeded the background value as well, creating a severe hazard for the environment (Timofeev et al., 2018). Furthermore, the highest tungsten concentration of samples in soils of central tungsten mines in Ganzhou was 318 mg/kg, approximately 62.4 times greater than the concentrations of Jiangxi background (Zheng et al., 2020). In contrast to most of the research focusing on the concentration analysis and pollutants level assessment of tungsten in the vicinity of tungsten mines, while few studies have been conducted to investigate the leaching characteristics and mechanisms of the tungsten-rich slags and sediments under special conditions.

In this study, two kinds of sequential extraction procedures (SEP) and batch leaching experiments on tungsten-rich slags and sediments were conducted to identify the release characteristics, the pollution and ecological risks of tungsten-rich samples under special conditions. In addition, the total concentrations of tungsten-rich samples were obtained with digestion. Considering that tungsten precipitates as a tungstic acid under conventional digestion conditions, various digestion methods were performed to determine the applicability and accuracy.

2. Materials And Methods

2.1 Slag and sediment sampling

Tungsten-rich slags and corresponding sediment were respectively collected from the fields adjacent to tungsten mines in Chenzhou, located on the southmost of Hunan Province, China, which generated large amounts of tungsten slags annually. In addition to the influence of anthropogenic activities, tungsten-rich solids in the natural environment mainly derived from geothermal activities. Thus, ZZQ sample was collected from the Rehai geothermal field in Tengchong, emerged in the western Yunnan, China, which is the largest and most active geothermal area in Tengchong (Guo and Wang, 2012). The specific information of the samples was presented in Table 1. Slags were stored in tightly closed plastic bags filled with N₂ to prevent oxidization, while sediments were put into the dry ice storage bottle, and transported to the lab. Samples were stored at – 20 °C in refrigerator, dried, crushed and sieved through a 200-mesh nylon sieve.

Table 1
Specific information of the samples

Sample no.	Sampling location	Sampling area	Longitude	Latitude	Sampling type
YLC	Mine Smelter	Chenzhou	111.500110	27.772479	slag
WKK	Tailing Reservoir	Chenzhou	112.566218	25.507617	slag
ZN01	Zhennan Township	Chenzhou	112.614638	25.423286	slag
ZN02	Zhennan Township	Chenzhou	112.614638	25.423286	slag
ZN03	Zhennan Township	Chenzhou	112.614638	25.423286	slag
SP01	Shenping Village	Chenzhou	112.599773	25.434439	slag
SP02	Shenping Village	Chenzhou	112.597176	25.439065	sediment
ZZQ	Rehai geothermal field	Tengchong	98.43601	24.95104	sediment

2.2 Digestion experiment

Three digestion methods (Microwave digestion, High-temperature and high-pressure closed digestion (HHM), Mixture of H₂SO₄ and H₃PO₄) digestion were conducted to identify the influence of pH on the total tungsten concentrations in this study. The HHM initially followed (Liu et al., 2008) to determine the total tungsten concentrations. Meantime, this study adopt the modification according to (Bostick et al., 2018). Notably, after the high-temperature and high-pressure closed digestion, the pH of the solution were adjusted to the 8 by ammonia solution to maintain alkaline conditions, and prevented potential precipitation of tungsten oxide (WO₃.H₂O). EDTA was also added to increase the solubility of iron and aluminum (hydro)oxides, restraining the adsorption process. The details of the digestion were presented in Table 2.

Table 2
Procedures of the digestion

Mixture of H₂SO₄ and H₃PO₄ digestion
1 The 200 mg powder sample was accurately weighted and placed into a Teflon bomb.
2 2 mL mixture of H ₂ SO ₄ (2.5mol/L) and H ₃ PO ₄ (1mol/L) were added to the crucible.
3 The Teflon bombs were placed into steel sleeve and heated at 90°C in oven for 5 h.
4 The solution was transferred to a polyethylene bottle, and diluted it with 2% HNO ₃ to 100 g.
High-temperature and high-pressure closed digestion
1 The 50 mg powder sample was accurately weighted and placed into a Teflon bomb.
2 A few drops of ultrapure water were added, then 1 mL HNO ₃ as well as 1 mL HF were added to the crucible in certain order.
3 The Teflon bombs were placed into steel sleeve, and heated at 190°C in oven for 48 h.
4 When the pressure vessel was cool, opening the cover and putting it on an electric heating plate (115°C) to evaporate the solution (Make sure the crucible wall was free of liquid). If there was black suspended matter, adding a few drops of HClO ₄ after evaporation, drying again.
5 Teflon bomb was added 3mL 30% H ₂ O ₂ and placed in the steel sleeve, heating at 190°C in oven for 12 h.
6 The pH values of the solution were adjusted to 8 by ammonia solution and added to 10mL 2M EDTA, diluting it with 2% HNO ₃ to 100 g and storing for ICP-MS testing.
Microwave digestion
1 The 50 mg powder sample was accurately weighted into the 50 mL vessel made of chemically modified polytetrafluoroethylene (PTFE).
2 20 mL sodium hydroxide solution (25g/L) was added to the container and the vessel was heated at 180°C for 30 min at 1000 W.
3 The solution was transferred to a polyethylene bottle, diluted it with 25g/L NaOH to 100 g and stored for ICP-MS testing.

2.3 Sequential extraction procedures

Tessier and Wenzel SEPs were conducted to analyze the specific fractions of tungsten in the samples. The procedures, reagents used, centrifugal time and temperature were listed in Table 3. Specifically, the dried and grounded samples were placed into 50 mL centrifuge tubes. After each constant temperature shock and centrifugation, the supernatant were taken out and put into a 50 mL colorimetric tube with deionized water for volume measurement. When it was well

combined, the supernatants were sampled and filtered through 0.22 µm filter membrane for subsequent analysis to calculate the recovery rate.

Table 3
Details of sequential fractionation procedures

Metal fraction	Extractive reagents	Time and temperature
Procedure 1: Wenzel et al. (2001)*		
W1: non-specifically sorbed	0.05 M (NH ₄) ₂ SO ₄	4 h, 25 °C
W2: specifically sorbed	0.05 M NH ₄ H ₂ PO ₄	16 h, 25 °C
W3: amorphous hydrous oxides bound	0.2 M NH ₄ -oxalate buffer in the dark (pH = 3.25)	4 h, 25 °C
W4: crystalline hydrous oxides bound	0.2 M NH ₄ -oxalate buffer + 0.1 M ascorbic (pH = 3.25)	0.5 h, 96 °C
W5: residual	HF–HNO ₃ –HClO ₄ (v/v/v = 1: 3: 2)	48h, 180 °C
procedure 2: Tessier et al. (1979)		
T1: water soluble/exchangeable	1.0 M MgCl ₂ (pH = 7)	1 h, 25 °C
T2: carbonates bound	1.0 M NaAc in 25% HAc (pH = 5)	5h, 25 °C
T3: Fe/Mn oxides bound	0.04 M NH ₂ OH·HCl in 25% HAc (pH = 2)	6 h, 96 °C
T4: organic matter bound	0.01 M HNO ₃ /30% H ₂ O ₂ (pH = 2)	2h, 85 °C
	30% H ₂ O ₂ (pH = 2)	3 h, 85 °C
	3.2 mol L ⁻¹ NH ₄ OAc in 20% HNO ₃	0.5h, 25 °C
T5: residual	HF–HNO ₃ –HClO ₄ (v/v/v = 1: 3: 2)	48h, 180 °C
*: Before the determination, the pH of each supernatant obtained from the SEPs should be adjusted to 8 by ammonia solution and appropriate amounts of EDTA should be added to the supernatant to prevent the potential precipitation of tungsten-bearing minerals under acid conditions.		

2.4 Batch leaching experiment

To investigate the effect of pH on the leaching behavior, the batch leaching experiments were conducted at the heated thermostatic water bath, which could provide constant temperature and agitation to ensure adequate contact between samples and soaking solution. The simulated rainfall was made up of nitric acid as well as sulfuric acid 4:1 mixed with purified water (the pH values of acid rain were 4.0 in accord with the local conditions). 5 g of samples and 200 mL of soaking solution were added to high-density polyethylene bottles to ensure the solid-liquid ratio of 1:40. On the contrast, the leaching solution was also adjusted to pH of 8.0 by sodium hydroxide solution. The batch lab experiments were conducted at 25 °C and 120 rpm in heated thermostatic water bath for 50 days. In addition, the samples were collected before placing in heated thermostatic water bath and shaking for a day. 10 mL supernatant respectively was collected at specific sampling times (i.e., 1, 2, 5, 15, 20, 25, 30, 35, 40, 45 and 50 days). Conductivity and pH values were determined, then the samples were filtered through 0.22 µm pore-size cellulose-acetate membranes and stored in centrifuge tubes for later analysis.

2.5 Sample analysis and characterization

X-ray diffraction (XRD) was used to analyze the mineralogical identification of solid samples, operating at 20 KV and 5 mA with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), and the results were presented in the θ -2 θ mode with 2 θ between 3° and 70° as well as a 2 θ step of 0.01°. Samples were also analyzed with a FEI Quanta200 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray (EDX) analytical capability.

The concentrations of W, As, Sb, Mn, Na, K, Ca, Mg, Li, Sr, Ba, Al, Fe, Si, B and Se in the filtrate were analyzed by ICP-MS (Nexion350D, PerkinElmer). The SO_4^{2-} , Cl^- , F^- and Br^- concentrations were determined by IC (ICS-900, Thermo Fish). All the pH measurements were performed by a Mettler Toledo pH meter. All the experiments in this study were run in duplicates for quality control. The average values of the measurements were reported.

3. Results And Discussion

3.1 Mineral composition of samples

The XRD patterns of slag and sediment samples were plotted in Fig. 1. The results showed that the slag and sediment samples mainly contained quartz (SiO_2), calcite (CaCO_3), fluorite (CaF_2) and dolomite $\text{CaMg}(\text{CO}_3)_2$ except for the samples of YLC and SP02, which were in the amorphous forms. However, tungsten-bearing minerals were not appeared, which may be attributed to the low tungsten concentrations or tungsten being adsorbed on the surface of other minerals.

3.2 The total concentrations of tungsten in slags and sediments by various digestion

The total concentrations of tungsten obtained with different methods were shown in Table 4. The highest mean concentration of tungsten, within all the slag samples, was 211.8 mg/kg of the ZN01 sample. In the case of the sediment samples, ZZQ sample owned the highest concentrations of tungsten was 378.1 mg/kg. Meantime, SP02 sediment sample also obtained a relatively high concentration of tungsten was 307.9 mg/kg. It is worth noting that the tungsten concentrations of the samples obtained by three digestion methods varied greatly, with the highest tungsten concentrations employed by the high-temperature and high-pressure closed digestion, the middle tungsten concentrations obtained by the mixture of sulfuric acid and phosphoric acid digestion, and the lowest tungsten concentrations from the microwave digestion.

Table 4
The total contents of tungsten obtained with different digestion methods

Sample no.	Mixture of H ₂ SO ₄ and H ₃ PO ₄ digestion(mg/Kg)	Microwave digestion (mg/Kg)	High-temperature and high-pressure closed digestion(mg/Kg)
ZN01	254.0	98.57	282.9
ZN02	85.82	61.74	98.23
ZN03	104.5	93.38	135.4
SP01	10.13	75.05	70.51
SP02	211.1	367.1	345.6
WKK	167.5	139.3	187.5
YLC	62.96	56.86	80.18
ZZQ	380.2	296.9	457.1

In this study, the microwave digestion with sodium hydroxide solution was used to obtain the total concentrations of tungsten in the samples, mainly based on the industrial method of alkaline decomposition method of tungsten ores. There were two main reasons for the low efficiencies of microwave digestion. One is, although digestion, under alkaline conditions, can prevent the precipitation of tungstic acid in solution, tungsten derived from the sample lattice can not be completely dissolved, resulting in lower tungsten digestion concentrations. In addition, the digested iron, manganese and aluminum could form (hydro)oxide precipitates under the alkaline conditions and further absorb amounts of tungsten in the solutions, which have demonstrated that the iron, manganese and aluminum (hydro)oxides in environmental were the main tungsten scavengers (Nan et al., 2009; Hh and Rjr, 2016; Rakshit et al., 2016). Thus, the tungsten concentrations in the slags and sediments obtained by microwave digestion with sodium hydroxide solution was far underestimated.

Another digestion method using mixture of sulfuric acid and phosphoric acid reported by (Zhao and Li, 2014) was also conducted to determine the total tungsten in slags and sediments. The tungsten digestion by this method could exist in the form of soluble phosphotungstic acid, preventing the precipitation of tungstic acid. Chen (Chen et al., 2020) demonstrated the leaching efficiencies of tungsten may reach approximately above 90% under the experimental conditions.

In addition, this method had very high efficiencies and short extraction time. This method is suitable in the case of ore grade of the samples with high grade of scheelite ore, which was expressed by Eq. (1). However, the ore grade of the samples were all below 1%. The leaching efficiencies of this method was reduced due to the high concentrations of impurity.



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Above all, there are few methods suitable for the digestion of tungsten-rich slags and sediments. Therefore, the modification for the high-temperature and high-pressure closed digestion in this study looks like necessary. In the modified digestion method, the samples were first completely digested by the conventional high-temperature and high-pressure method. Then, the solution pH was adjusted with an ammonia solution, creating an alkaline condition that

prevented the precipitation of tungstic acid. Meantime, EDTA was also added to the digestion solution, as a complexing agent, which increased the solubility of iron and aluminum (hydro)oxides in the alkaline solution. Ultimately, the more objective total tungsten concentrations in the slags and sediments were obtained, which provided a basis for further determination of tungsten concentrations in solid samples.

3.3 Chemical partitioning of tungsten-rich samples with two SEPs

The mobility, bioavailability, toxicity, migration and geo-chemical cycle of tungsten not only depend on their total concentrations but also on their specific chemical forms, and on their binding state (precipitated with primary or secondary minerals, complexed by organic ligands, and so on) (Filgueiras et al., 2002; Gleyzes et al., 2002). SEPs, owning high accuracy and wide application, are commonly employed for exploring solid chemical forms to evaluate the adverse environmental impacts of tungsten-rich samples.

3.3.1 Tungsten fractions extracted by the Tessier SEP.

Firstly, the tungsten recovery rates of Tessier SEP ranged from 84.5–118.4%, which was reasonable for further fractionation analysis. The chemical fractions of tungsten in the samples with the Tessier SEP were shown in Fig. 2a. It should be noted that the residual fraction accounted for more than 90% of the total tungsten in most samples except for the samples ZN01 and YLC with the Tessier SEP. Among them, the total mass residual fraction of tungsten in the samples SP02 and WKK were up to 98.6% and 97.4%, while the oxidizable fraction of tungsten in the ZN01 sample accounted for 68%, which was the only sample that the oxidizable fraction exceeded the residual fraction. Another special case was the YLC sample, containing about 7% of the carbonate fraction and 9% of the reducible fraction.

3.3.2 Tungsten fractions extracted by the Wenzel SEP

The Wenzel SEP is a modification of the Tessier SEP and possesses a more specific tungsten distribution pattern. The tungsten recovery rates of Wenzel SEP for 7 samples were between 82.1% and 115.7%, and the corresponding chemical fractions of tungsten using the Wenzel SEP were shown in Fig. 2b.

The non-specially absorbed tungsten fraction, extracted by ion-exchange processes, usually represents weakly-adsorbed species, which is most readily released into the environment. It is comforting that, apart from the ZN03 sample, the percentages of exchangeable fraction of tungsten in other samples are very low and almost can negligible by both the Wenzel SEP and Tessier SEP. The specifically absorbed fraction indicates the tungsten precipitation or coprecipitation with carbonate, which could only can be detected in the ZN03 sample, accounting for 2.4% of the total mass fractions. Specifically absorbed fraction is sensitive to pH, meaning that the tungsten can be released by the vary of environmental pH. The amorphous hydrous oxides bound fraction, in the third step, considers the tungsten bound to amorphous iron and aluminum oxides, ranging 1.11–38.34%. The crystalline hydrous oxides bound fraction represents the tungsten bound to crystalline iron and aluminum oxides, in a range of 4.8–47.95%. Primary and secondary minerals contained metals in the crystalline lattice constitute the bulk of the residual fraction, which can be destructed by strong acids, such as HF, HClO₄, HCl and HNO₃ (Gleyzes et al., 2002). This tungsten fraction is always considered to be the most difficult to move and the least potentially harmful. It accounts for more than 36% for most samples except the ZZQ sample, which only contains 4.8% of residual fraction.

3.3.3 Comparison of two sequential extraction procedures

The percentages of non-specifically and specifically absorbed tungsten fractions in two SEPs were very low, while the distribution of hydrous oxides bound fraction and residual fraction were distinctly different. Notably, the proportions of the tungsten in the residual fraction significantly affected by the incomplete extraction of the previous step. Hence, the

main reason for the difference were mostly attributed to the extraction efficiencies of the amorphous hydrous oxides bound fraction and crystalline hydrous oxides bound fraction of tungsten.

Compared to the Tessier SEP, the ascorbic acidic/ammonium oxalate reagent using in the Wenzel SEP can dissolve completely crystalline Fe oxides and does not attack silicates(Li et al., 2019b), therefore it was more accurate for extracting the Fe and Al oxides bound fractions of tungsten. Meantime, the previous digestion results showed that the samples owned high concentrations of Fe, Mn and Al, which may result in a high proportions of tungsten bound to iron and aluminum (hydro)oxides. In addition, the results of the Tessier SEP indicated that the mobility of samples were very low, and almost no tungsten can be leached out, which was contrary to the result of the leaching experiments in section 3.4. Due to the low tungsten concentrations of samples in section 3.4, while a part of tungsten were still released from the samples.

Consequently, Wenzel SEP was superior to the Tessier SEP in terms of extracting the amorphous hydrous oxides bound fraction and crystalline hydrous oxides fraction of tungsten in the samples. Hence, the Tessier SEP underestimated the proportions of Fe and Al oxides bound fraction of tungsten in the tungsten-rich slags and sediments and the environmental risks of tungsten.

3.4 The migration mechanisms of tungsten-rich samples by batch leaching experiment

The results have shown the different leaching mechanisms of samples, which were divided into three groups accordingly. Group I included ZN01, ZN02, ZN03, SP01, WKK, YLC sample, while SP02 and ZZQ samples were in Group II and Group III, respectively.

3.4.1 The leaching mechanism of Group I samples

The leaching characteristics of the Group I samples were shown in Fig. 3. It was observed that the tungsten concentrations in the leachate samples gradually increased, in the progress of leaching experiments. Under alkaline leaching conditions (pH = 8), the leaching rate of tungsten from Group I samples increased the fastest during the first 15 days, and then increased slowly until it reached equilibrium, while the highest leaching efficiency of most samples occurred within 25 days under acidic leaching conditions (pH = 4). In addition to the higher efficiency of alkaline leaching, higher leaching concentrations of tungsten at equilibrium were also obtained under alkaline conditions. The ZN03 sample possessed the highest leachate concentration of 87.09 µg/L when leached in a solution of pH 8, while under acid conditions, the highest leachate concentration of 56.79 µg/L occurred at 25 days for the ZN01 sample. It indicated that alkaline condition is more effective for the leaching of Group I samples.

The digestion experiment revealed high concentrations of Fe and Al were found in Group I samples. Meantime, the results of Wenzel SEP also showed that amorphous hydrous oxides bound fraction and crystalline hydrous oxides bound fraction of tungsten accounted for about 60% in Group I samples. Since the adsorption of tungsten by Fe and Al (hydro)oxides could be inhibited under alkaline solution(Gustafsson, 2003; Seiler et al., 2005; Xu et al., 2006; Steinberg et al., 2007; Dave and Johannesson, 2008; Nan et al., 2009; Sun and Bostick, 2015).

3.4.2 The leaching mechanism of Group II samples

The leachate concentrations of tungsten in the Group II were presented in Fig. 4. Although the digestion result indicated that the SP02 sample contained high concentrations of tungsten, the tungsten concentrations of the leachate maintained at very low level under acid or alkaline conditions. And the leachate tungsten concentration of the SP02 sample deceased with the progression of leaching experiment, approaching an equilibrium state at about 20

days. It was attributed to the high residual fraction of tungsten in the SP02 sample, which indicated the low mobility of tungsten from the SP02 sample. Therefore, SEP is of great significance in judging the potential risk of tungsten-rich samples, and the bioavailability, toxicity, migration and geo-chemical cycle of the tungsten not only depend on their total concentrations but also on their specific chemical forms and on their binding state (precipitated with primary or secondary minerals, complexed by organic ligands, and so on).

3.4.3 The leaching mechanism of Group III samples

As mentioned previously, the average total tungsten concentration of ZZQ sample conducting with different digestion methods, with a mean concentration of 378.1 mg/Kg, was the highest total concentration of tungsten in all samples. The results of SEP indicated that the amorphous hydrous oxides bound fraction as well as crystalline hydrous oxide-bound fraction of tungsten accounted for nearly 95%, meaning tungsten could be easily leached from the samples under experimental conditions. However, the leachate concentration of ZZQ sample was very low within the leaching period and the highest leachate tungsten concentration was only 4.874 $\mu\text{g/L}$. Meantime, in contrast to the alkaline leachate of other samples, the pH values of the ZZQ leachate ranged from 4.52–6.68, which maintained acid condition although the initial pH values was 4.0 or 8.0.

Hence, to investigate distinctly the leaching mechanism of ZZQ sample, another leaching experiment under alkaline condition was conducted to retain the pH values of the soaking solution at 8 by adding a small amount of sodium hydroxide solution every day. The results of twice leaching experiments were shown in Fig. 5. The leachate concentrations of tungsten were distinctly different in two experiments. The pH constant experiment indicated that the tungsten concentration in the leachate sample, gradually increased and reached up to 105.6 $\mu\text{g/L}$ at 50 days.

It was also attributed to the tungsten desorption onto iron and aluminum (hydro)oxides under alkaline conditions. In the previous discussion, alkaline conditions were not beneficial for tungsten adsorption by iron and aluminum (hydro)oxides, which was also confirmed by additional experiment with fixed pH values. Although the XRD pattern of the ZZQ sample did not show the diffraction characteristics of iron bearing minerals, the existence of iron-bearing minerals was found by the SEM, shown in Fig. 6. In general, the maximum adsorption of tungsten species on iron-bearing minerals occurs in the pH range 4–6 (Hingston et al., 1967), while only 50% and 10% of tungstates were still absorbed at neutral and above pH 10, respectively (Nan et al., 2009). Therefore, the tungsten absorbed on the surface of iron-bearing minerals would be released with the increasing environmental pH values. For the sediments contained high concentrations of iron and aluminum (hydro)oxides around the vicinity of tungsten ores or active geothermal area, it is necessary to avoid leaching of neutral or alkaline liquid, thus releasing cumulative amounts of tungsten into the water environment.

4. Conclusion

(1) The XRD patterns of solid samples indicated that the slag and sediment samples mainly contained quartz (SiO_2), calcite (CaCO_3), fluorite (CaF_2) and dolomite $\text{CaMg}(\text{CO}_3)_2$ except for the samples YLC and SP02, which were in the amorphous forms.

(2) The digestion results showed that the addition of ammonia solution and EDTA improved distinctly the efficiencies and obtained accurately the total concentration of tungsten. In addition, the high-temperature and high-pressure closed digestion can dissolve completely the residual fraction and applied to disposing the low ore grade of samples, providing a new idea for the further study. Compared to the results of two kinds of SEPs, Wenzel SEP was approximately better than the Tessier SEP to extract Fe and Al oxides bound fractions of tungsten due to the

availability of appropriated extraction reagents. Hence, the Tessier SEP underestimated the proportions of Fe and Al oxides bound fraction, and the adverse environmental impacts of tungsten.

(3) The batch leaching experiments demonstrated the leachate concentrations of tungsten in tungsten-rich samples were controlled by the desorption of iron and aluminum oxides, which were released more with the increasing environmental pH values. The findings of this study are expected to contribute to evaluating the leaching contamination and environmental risk assessment of tungsten-rich samples under the special conditions.

Declarations

Authorship contribution statement

Hongyu Song: Investigation, Methodology, Writing – original draft.

Yaowu Cao: Reviewing, Conceptualization, Editing.

Zheyang Miao: Contributed reagents, Materials

Hao Luo: Contributed reagents, Materials.

Qinghai Guo: Reviewing, Conceptualization, Editing.

Declarations of competing interest

The authors declare no conflict of interest in this study.

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Figures

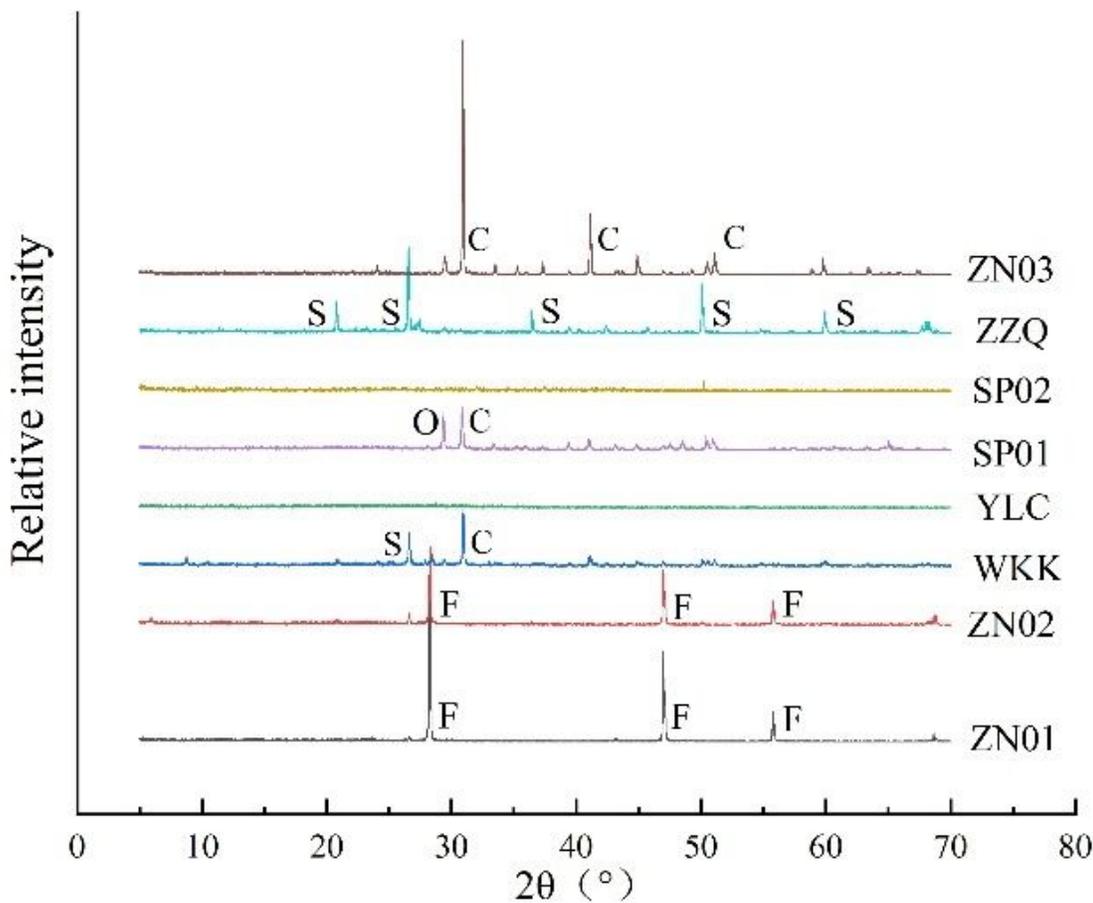


Figure 1

XRD patterns of slags and sediments C: calcite, S: quartz, O: dolomite, F: fluorite

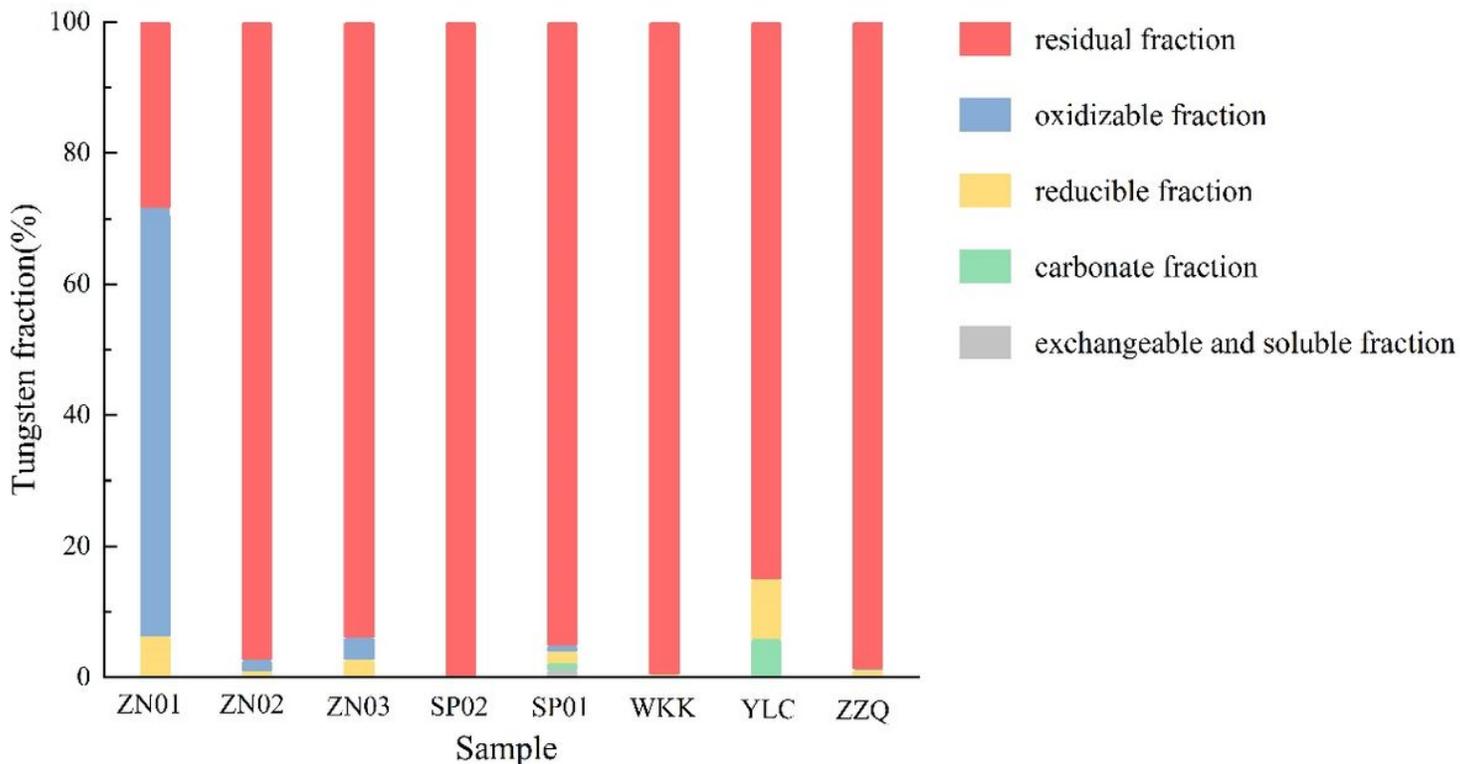


Figure 2

The tungsten fractions with Tessier method

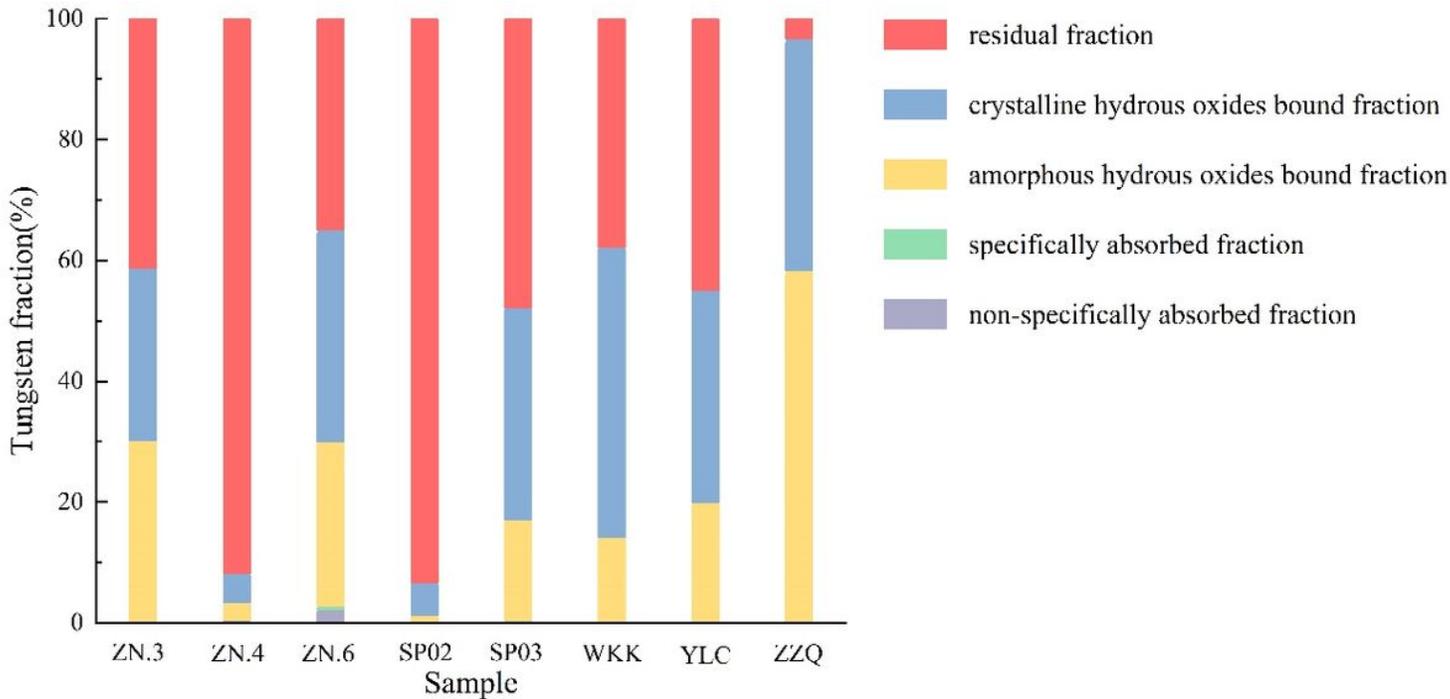


Figure 3

The tungsten fractions with Wenzel method

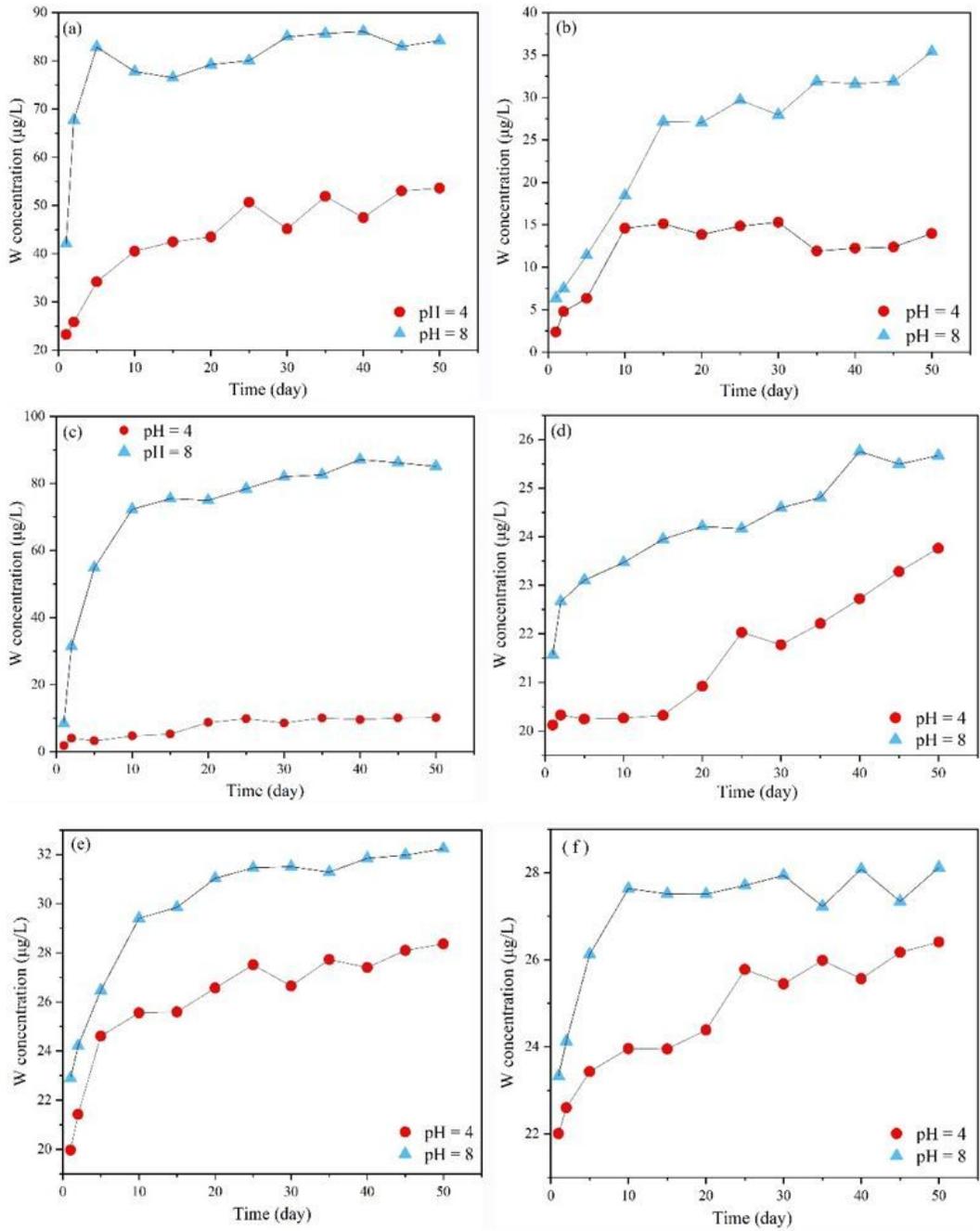


Figure 4

The leachate concentrations of tungsten in the Group I: (a) ZN01 (b) ZN02 (c) ZN03 (d) YLC (e) SP01 (f) WKK

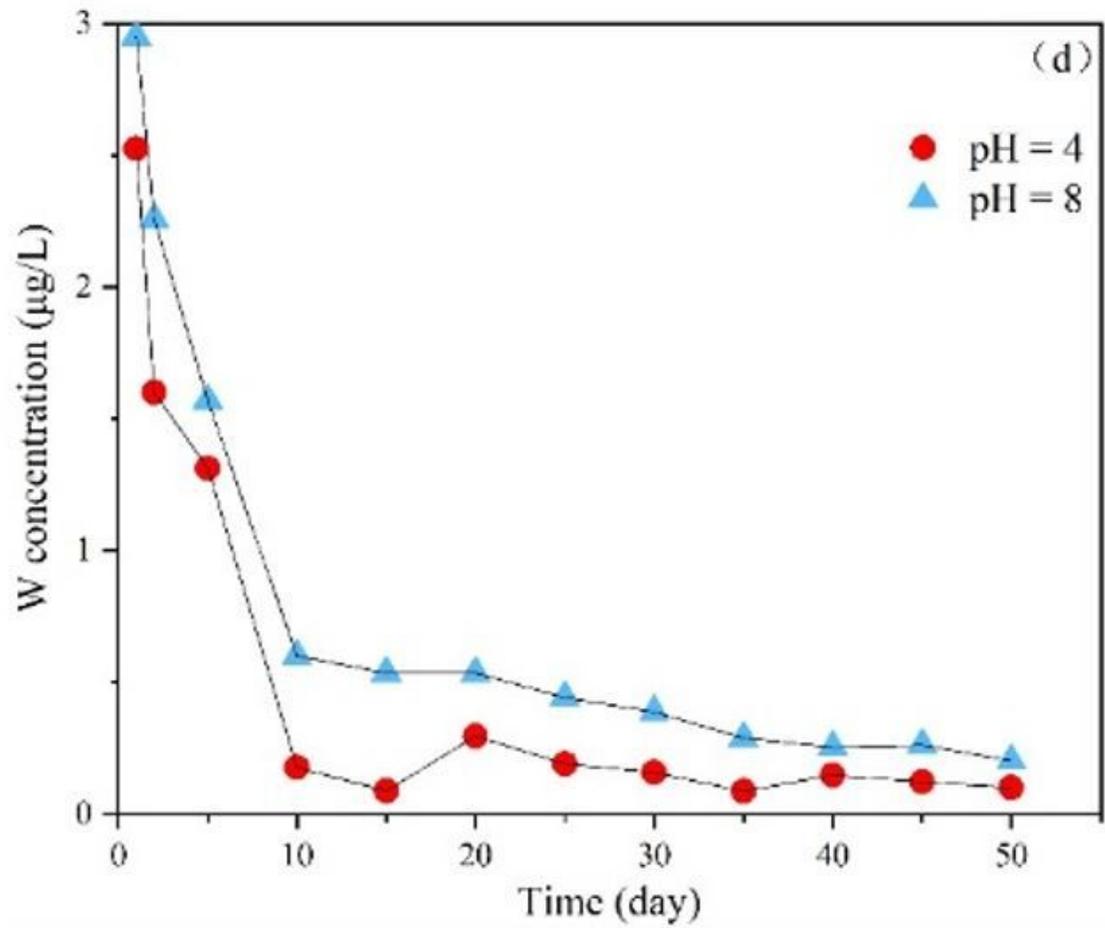


Figure 5

The leachate concentration of tungsten of the SP02 sample

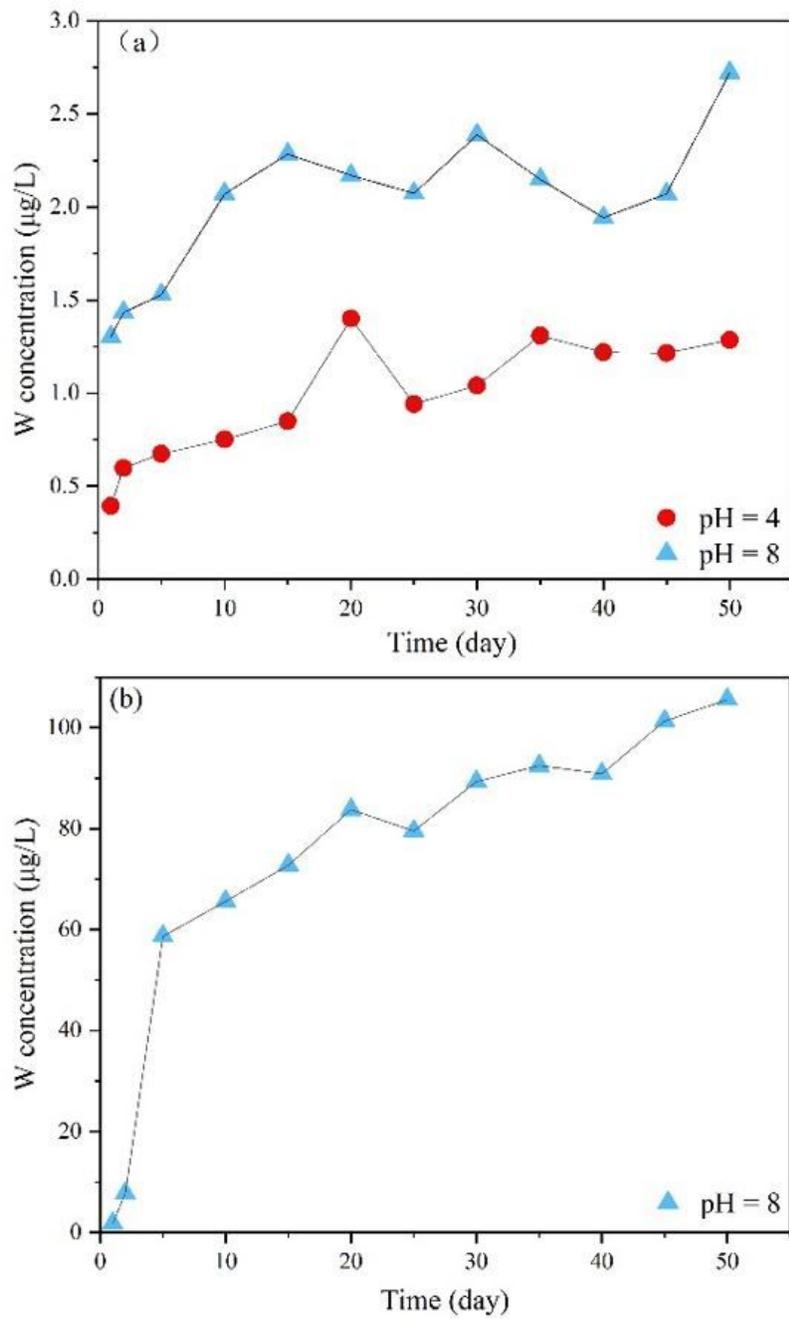
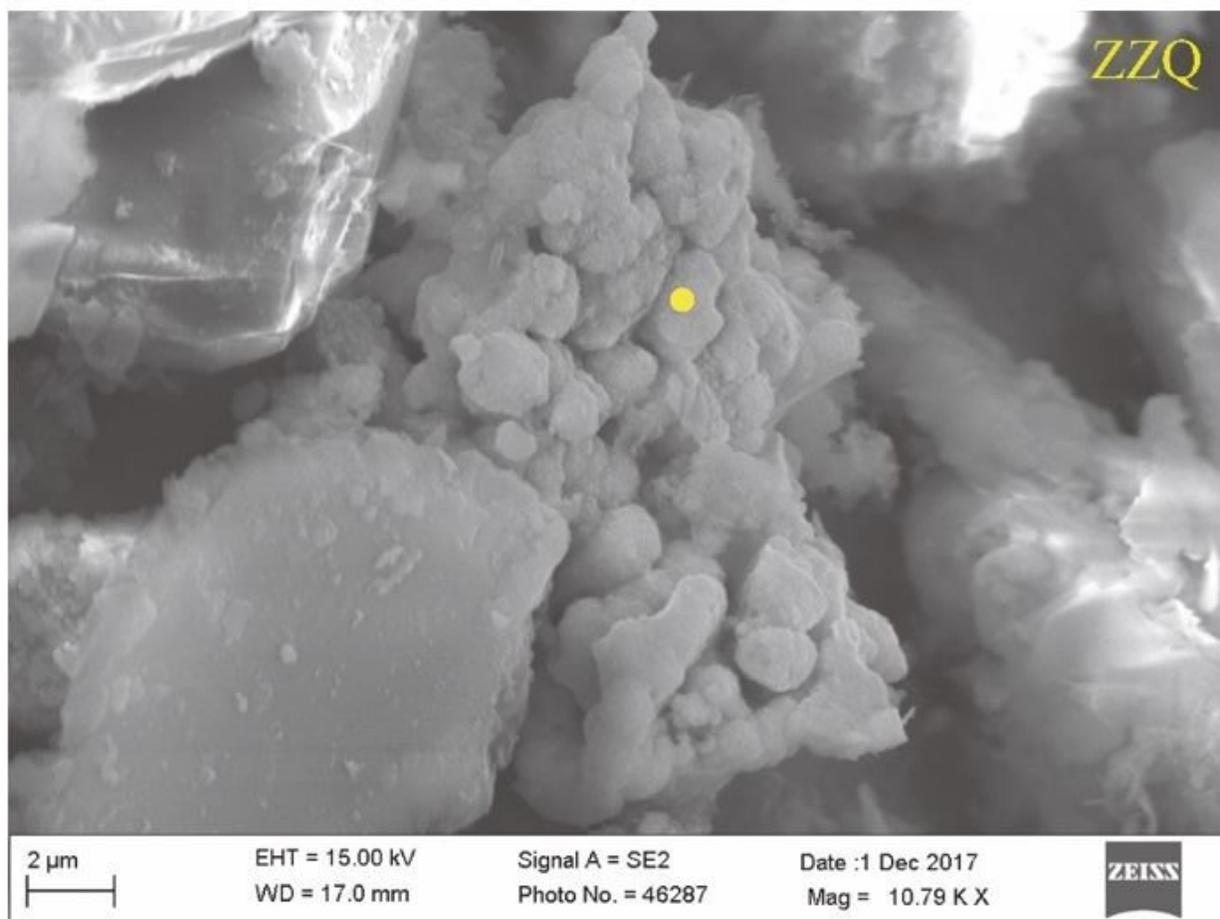


Figure 6

The leachate concentrations of tungsten of the ZZQ sample: (a) the first leaching experiment (b) additional experiment



Weight percent (%)

O	Fe	Si	P	Br
40.64	50.62	3.40	1.14	4.20

Figure 7

SEM image of the ZZQ sample