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Sustainable Optimization of Decomposition Conditions for Tungsten-Molybdenum Ores with Diverse Mineral Compositions

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Abstract

This study investigates various decomposition methods for tungsten-molybdenum ores—wet, dry, and autoclave—to identify optimal conditions for Mo and W extraction. Four ore samples were examined: two reference materials and two natural samples from Central Kazakhstan. Natural samples O-3 and O-4, classified as refractory silica-rich tungsten-molybdenum ores, have complex mineralogical compositions. Optimal decomposition conditions for these ores were established for the first time, considering their geochemical features. X-ray fluorescence (XRF) and X-ray diffraction (XRD) were used to determine the elemental and phase composition, while ICP-MS analyzed digested solutions. The efficiency of Mo and W extraction depend on both mineralogical form and matrix. Nine decomposition methods were tested. For standard molybdenum–tungsten ore samples (O-1 and O-2), the highest recoveries were achieved using acid-based techniques, particularly autoclave digestion with HNO_3-HF and wet digestion with HNO_3. In contrast, natural samples with complex silica-rich matrices containing Al, Fe, and Ca (O-3 and O-4) required stronger approaches such as autoclave treatment with HNO_3-HF or HCl and alkaline sintering with Na_2CO_3 followed by HNO_3 dissolution. All experiments were performed in triplicate, with a standard deviation of 3–5%. These findings demonstrate the importance of matching decomposition strategies to ore characteristics for effective Mo and W recovery.

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1. Introduction

The processing of tungsten and molybdenum ores represents a critical challenge in the metallurgical and mining industries, as these metals are widely used across various high-technology sectors, including aerospace, defense, and electrical engineering.[1-5] Tungsten and molybdenum ores are known for their complex mineralogy, which makes their processing both energy-intensive and costly. One of the key stages in the extraction of tungsten and molybdenum is sample preparation, where it is critical to consider the diverse chemical and physicochemical properties of these materials. Efficient recovery of these metals depends on ore type, the presence of impurities, and the mineralogical characteristics of key phases such as wolframite and molybdenite.[6-8] These challenges necessitate the application of advanced technologies that can significantly enhance metal recovery, reduce operational expenses, and minimize environmental impact.

Globally, a wide range of decomposition methods is employed for the treatment of tungsten-molybdenum ores, including acid leaching, alkaline treatment and sintering with salts, two−stage acid decomposition, solvent extraction, and selective precipitation techniques.[9-12] Each method has distinct advantages and limitations. For instance, mixed acid decomposition using concentrated acids (HCl, HNO_3, HF) is effective for complex silicate ores but requires intricate sample preparation and stringent control of process conditions.[13,14] Alkaline or salt sintering effectively decomposes stable mineral matrices but leads to elevated concentrations of alkali components in solution, which complicates subsequent analysis and the recovery of target elements.[15] Selective precipitation and dissolution are primarily used for separating macro amounts of tungsten and molybdenum, though they require precise control of pH and redox potential.[16] To enhance separation efficiency, extraction schemes involving

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peroxide or organic complexing agents are also employed.[17]

Recently, increased attention has been paid to the optimization of sample preparation strategies for trace and major element analysis in complex ores.[18-20] Advanced instrumental methods, such as ICP-MS and ICP-OES, require reliable decomposition protocols that ensure complete digestion of refractory mineral phases without introducing matrix effects. This is particularly relevant for Mo-W ores, where target elements may be locked in silicates, sulfides, or scheelite-molybdate phases.[21-25] Therefore, refining digestion procedures becomes essential for accurate geochemical characterization and metallurgical assessment.

Most of the research focuses on a single method of converting ore into solutions. This study complements previous works by comparing and integrating several methods of decomposition of tungsten- and molybdenum-containing natural ores. Nine processing techniques were evaluated at four different ore sites, including natural samples with complex mineralogical composition from Central Kazakhstan.

The decomposition of tungsten and molybdenum ores is typically carried out using dry, wet, or autoclave techniques.[26] Wet decomposition, involving readily available acids, is effective for extracting metals from sulfide and refractory minerals. It is relatively simple to implement, energy-efficient, and does not require high temperatures or pressure. However, strict adherence to safety protocols is essential. In dry methods such as sintering, ores are treated at high temperatures in a muffle furnace with fluxes, and the resulting sinter is subsequently dissolved in acids. This approach is suitable for ores resistant to direct acid decomposition. Autoclave decomposition is performed under elevated temperature and pressure using acidic or oxidative media, which accelerates reactions and enhances metal recovery, especially from molybdenum ores. While the autoclave method offers high efficiency, process control, and potential environmental advantages, it requires specialized equipment and substantial energy input, making it ideal for small to medium-scale processing of complex ores. These techniques are fundamental for converting metals into soluble forms. Despite the availability of various technologies, the decomposition of such ores remains a complex task, requiring continued innovation and optimization.[27,28]

The aim of this study is to evaluate different decomposition methods and determine the optimal conditions for maximizing leaching efficiency for molybdenum and tungsten. A key aspect of the work is the use of advanced analytical techniques to characterize natural samples before and after decomposition, allowing for precise quantification of target metals. Unlike previous studies, this research includes a comparative analysis of nine decomposition schemes applied to four different ore types, enabling a more tailored approach based on mineralogical composition. The findings will contribute to identifying optimal processing parameters for maximizing metal recovery, thereby enhancing the overall efficiency of tungsten-molybdenum ore processing in metallurgical operations.

2. Materials and methods

2.1 Materials

Reagents of high purity, suitable for trace-level analysis, were used in this study. Nitric acid (HNO_3, 65.0 wt%, Suprapur, Merck, Darmstadt, Germany) and hydrochloric acid (HCl, 30.0 wt%, Suprapur, Merck) had a purity grade of ≥99.9% and were certified for ultrapure metal analysis, containing less than 0.1 ppb of impurities. Hydrogen peroxide (H_2O_2, 30.0 wt%, analytical grade, Sigma-Aldrich) was used for the oxidative decomposition of sulfide minerals. Aqueous ammonia ($NH_3 \cdot H_2O$, 25.0 wt%, Suprapur, Merck) was employed as a selective precipitant for iron during solution purification. Hydrofluoric acid (HF, 40.0 wt%, analytical grade, KazpharmLab, Kazakhstan) was used for the decomposition of silicon-containing ores and concentrates. Anhydrous sodium carbonate (Na_2CO_3, ≥99.9%, analytical grade, Panreac; supplied by KazpharmLab) was used as a flux for sintering in a muffle furnace. All water used in the experiments was deionized (18.2 MΩ·cm, Milli-Q system). Laboratory glassware was pretreated by soaking in a 10.0% nitric acid solution and thoroughly rinsed with deionized water.

2.2 Sample preparation

Four samples were used in the study: two certified reference materials-molybdenum ore containing 0.32% Mo (GSS 1719-79)[29] and tungsten concentrate containing 56.89% W_2O_5 (GSS KSh(t) 3460-86)[30] as well as two natural ore samples collected from Central Kazakhstan (molybdenum and tungsten ores). The abbreviations of the research objects are presented in Table 1.

The elemental composition of the standard concentrates O-1 and O-2 is as follows: concentrate O-1 contains WO_3 − 0.024 %, Mo − 0.32 %, Pb − 0.014 %, and BeO − 0.022 %. For concentrate O-2, the values are WO_3 − 56.89 %, Mo − 0.0326 %, S − 0.341 %, P − 0.165 %, and Cu − 0.012 %.

Initial crushing of the ores was performed using a jaw crusher (JSC "Mechanobr-Tekhnika," serial no. 157/8/1, 2008, St. Petersburg, Russia). Further grinding to a powder state was conducted using a vibration mill (IVP-100) followed by an agate mortar.

Table 1: Abbreviations of research objects.

Research Objects	Abbreviation
Mo ore 1719	O-1
W ore 3460	O-2
Natural ore sample 1	O-3
Natural ore sample 2	O-4

2.3 Characterization methods

X-ray fluorescence (XRF) analysis was performed using an X-Supreme 8000 analyzer (Oxford Instruments, UK) equipped with a high-resolution Si-PIN detector. The instrument operates with a 10 W X-ray tube at up to 50 kV.

X-ray diffraction (XRD) analysis was conducted in powder diffraction mode using a TD-3700 diffractometer (Tongda, China) with a copper anode (λ = 1.5406 Å, Cu Kα radiation). Samples were ground to a fine powder, uniformly applied to a sample holder, and scanned in θ-2θ mode at room temperature over a range of 10°-80° 2θ, with a step size of 0.0188°. Phase identification was performed using the PDF-2 database (ICDD). Microwave-assisted decomposition of molybdenum-containing samples was carried out in a closed system using a SpeedWave Four digestion system (Berghof, Germany) equipped with DAP-60+ autoclaves (Berghof, Germany).

2.4 Decomposition procedures

Method 1 – Open-system decomposition using hydrochloric acid and hydrogen peroxide (3:1). A 0.1 g sample was placed in a beaker, and a mixture of hydrochloric acid and hydrogen peroxide was added. The oxidizer was introduced dropwise to enhance dissolution. The mixture was heated nearly to boiling (without boiling), and distilled water was added until the white fumes disappeared. After cooling to room temperature, hot ammonium hydroxide was added to precipitate iron. The solution was filtered, transferred to a 50 mL volumetric flask, and diluted to the desired volume.

Methods 2 and 3 – Open-system decomposition using 2 M nitric acid or hydrochloric acid. A 0.1 g sample was placed in a beaker, followed by the addition of nitric acid (or hydrochloric acid). The mixture was heated to maximum dissolution without boiling. After adding water until the fumes disappeared, the solution was cooled, filtered, transferred to a 50 mL volumetric flask, and diluted to the mark.

Methods 4 and 5 – Dry decomposition (sintering) with subsequent dissolution in nitric or hydrochloric acid. To 0.1 g of ore, 0.2 g of sodium carbonate was added and placed into a platinum crucible. The mixture was fused in a muffle furnace at various temperatures. A water-soluble cake was obtained only at 900 °C. After cooling in a desiccator, the cake was dissolved in nitric acid, filtered, and the resulting solution was diluted to 50 mL.

Method 6 – Autoclave decomposition using nitric acid and hydrogen peroxide. A 0.1 g sample was placed in an autoclave, followed by 7 mL of concentrated nitric acid and 2 mL of hydrogen peroxide. After decomposition, the solution was cooled, filtered if necessary, and diluted to 50 mL.

Method 7 – Autoclave decomposition using ammonium hydroxide. A 0.1 g sample was mixed with 9 mL of ammonium hydroxide in an autoclave. After decomposition, the solution was cooled, filtered if necessary, and diluted to 50 mL.

Method 8 – Autoclave decomposition using nitric and hydrofluoric acids. A 0.1 g sample was treated in an autoclave with a mixture of 4 mL nitric acid and 5 mL hydrofluoric acid. The solution was cooled, filtered if a precipitate was present, and diluted to 50 mL.

Method 9 – Autoclave decomposition using concentrated hydrochloric acid. A 0.1 g ore sample was treated with 9 mL of concentrated hydrochloric acid in an autoclave. After decomposition, the solution was cooled, filtered if necessary, and diluted to 50 mL.

The autoclave processing parameters for methods 6-9 are presented in Table 2.

2.5 Elemental analysis of samples

Following decomposition and solution preparation, 2 mL aliquots were taken from each sample solution for elemental analysis. Samples were further diluted to achieve target element concentrations around 500 µg/L. The concentrations

Table 2: Conditions for decomposition of molybdenum-tungsten-bearing samples.

Types of Decomposition	Method, №	Reagents	Precipitant NH_4OH	Decomposition Parameters	Time, min
Wet Method in an Open System	1	$HCl + H_2O_2$ (3:1)	+	t=80°C	120
	2	HNO_3	–	t=80°C	120
	3	HCl	–	t=80°C	120
Dry Method by Sintering	4	Na_2CO_3 followed by dissolution in HNO_3	–	t=900°C	120
	5	Na_2CO_3 followed by dissolution in HCl	+	t=950°C	10
Autoclave Method in a Closed System	6	HNO_3, H_2O_2	–	t=80°C, P=20 bar, ramp=5	20
	7	NH_4OH	–	t=75°C, P=80 bar, ramp=5	35
	8	HNO_3, HF	–	t=175°C, P=80 bar, ramp=5	30
	9	HCl к.	–	t=75°C, P=80 bar, ramp=5	25

Note: "+" indicates use of ammonium precipitant; "–" indicates no ammonium precipitant was used.

of molybdenum and tungsten were determined using inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7500a spectrometer (Santa Clara, CA, USA). For accurate measurements, calibration standards were prepared in the range of 5 to 1000 µg/L, divided into subranges, using a certified multi-element calibration solution (Multi-Elemental Calibration Standard-4).

3. Results and discussion

Given the complex mineralogical and chemical composition of tungsten-molybdenum ores, the development of an effective decomposition strategy requires a detailed understanding of both the phase composition and the behavior of target elements under different treatment conditions. This section presents a comprehensive analysis of the chemical and mineralogical properties of four ore samples and evaluates the performance of nine decomposition methods, including wet acid leaching, dry sintering, and autoclave digestion. The primary objective is to identify the most efficient conditions for extracting molybdenum and tungsten, considering the refractory nature of specific mineral phases. By correlating analytical data from XRF, XRD, and ICP-MS with the decomposition outcomes, this study aims to establish a matrix-dependent approach for processing Mo-W ores. The results serve not only to optimize sample preparation for trace and bulk analysis but also illuminate the broader applicability of each decomposition route, enabling informed selection of technologies for industrial scale implementation. This section is structured to first explore the elemental and mineralogical composition of each sample, which forms the basis for selecting appropriate digestive methods. Subsequent subsections detail the effectiveness of each technique, with particular attention to the influence of ore matrix characteristics on recovery rates. Finally, a comparative evaluation with literature data is presented to contextualize the findings and highlight the practical advantages of the selected approaches.

3.1 Investigation of the chemical composition of samples

To determine the elemental composition of natural samples, an X-ray fluorescence (XRF) analyzer was employed. The obtained results are presented graphically in Fig. 1. The XRF results (Fig. 1) for samples O-3 and O-4 show that the major elements include Si, O, Fe, F, Na, Al, K, and Ca. A particularly high silicon content may complicate ore opening due to the formation of quartz "shells."

It is important to note that ore classification based on the content of valuable components allows for distinguishing between low-grade and high-grade ore, which is a key factor in selecting the appropriate processing technology. Molybdenum ores are considered high-grade when the Mo content is 0.2-0.3% or higher, whereas ores with 0.05-0.1% or lower are classified as low-grade. As for tungsten ores (converted to tungsten oxide, WO_3), samples with 1.0-1.5% and above are regarded as high-grade, while those with 0.3-0.5% and below are low-grade. In our study, samples O-1 and O-3 were rich in molybdenum, whereas O-2 and O-4 were poor. In terms of tungsten, only sample O-2 exhibited significant content, while the remaining samples were classified as tungsten-poor. Such classification allows for accurate assessment of the industrial value of raw materials and supports the selection of the most effective and economically viable processing methods.

To determine the mineralogical and phase composition, X-ray diffraction (XRD) analysis was conducted (Fig. 2-5).

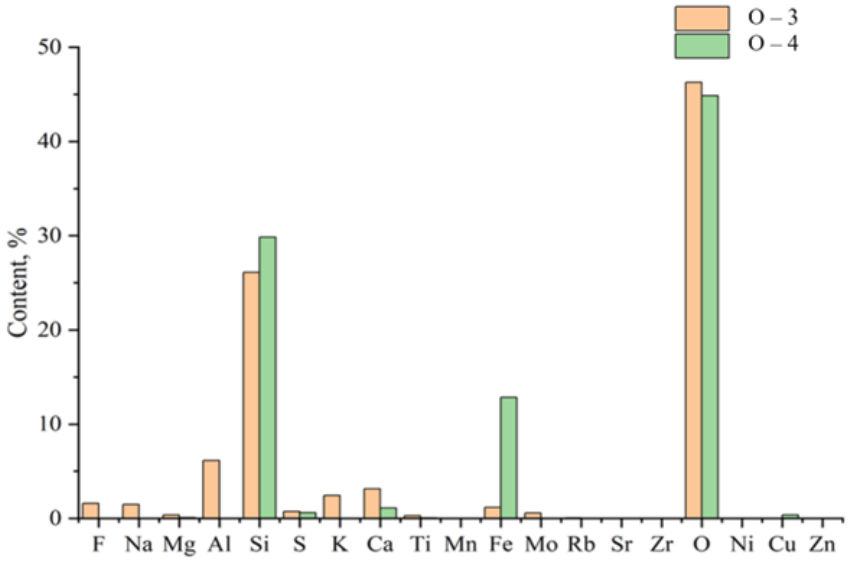

Fig. 1: XRF Analysis results of the ore samples.

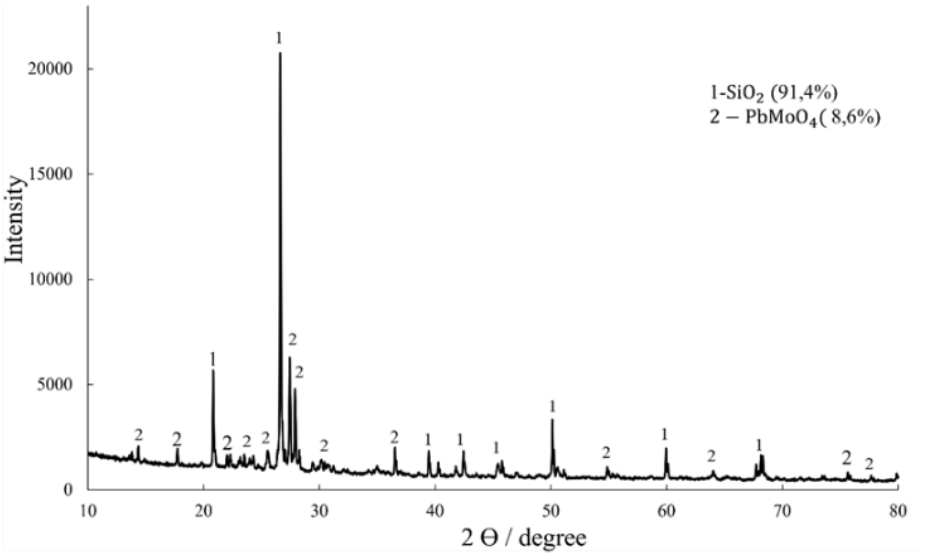

Fig. 2: Mineralogical composition of sample O-1.

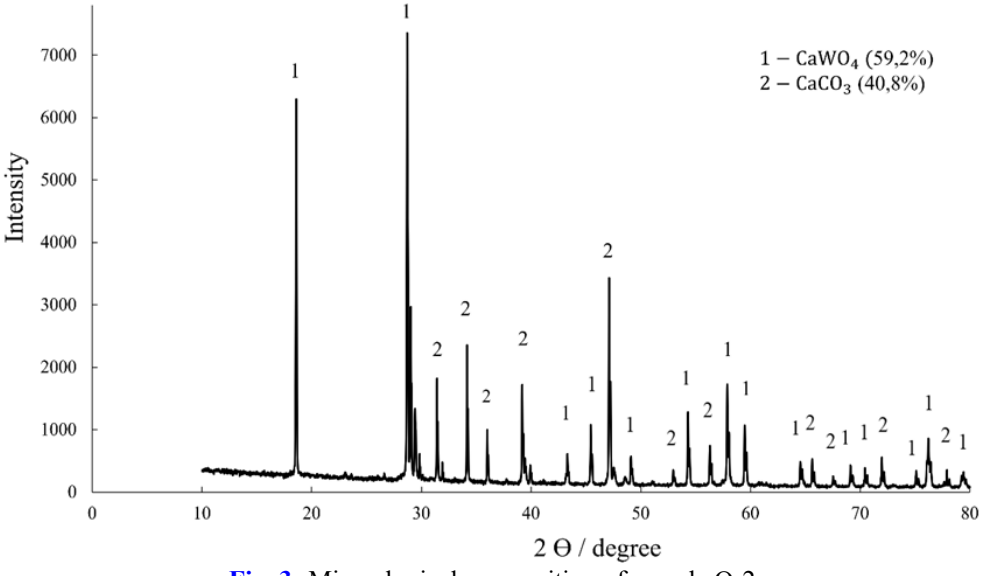

Fig. 3: Mineralogical composition of sample O-2.

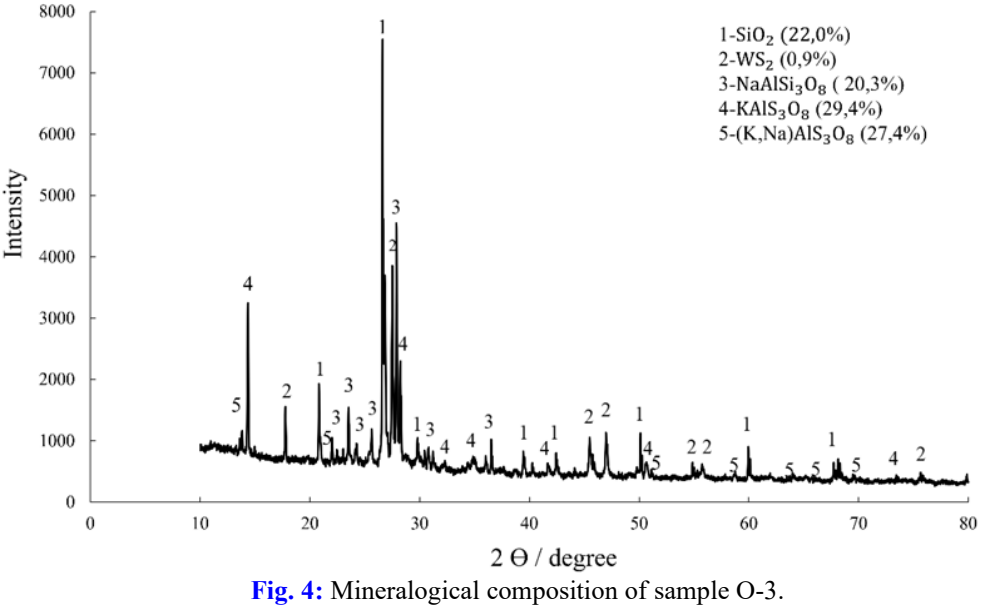

Fig. 4: Mineralogical composition of sample O-3.

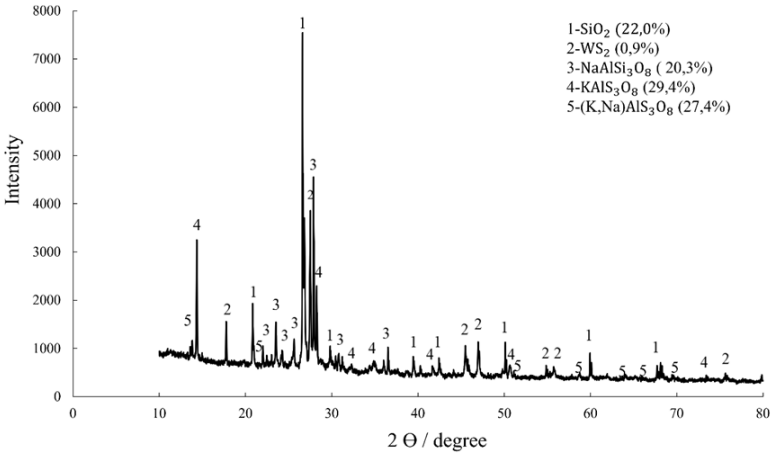

Fig. 5: Mineralogical composition of sample O-4.

The XRD pattern of Sample O-1 reveals distinct peaks corresponding to crystalline quartz (SiO_2), which dominates the composition at 91.4%. Additionally, $PbMoO_4$ (scheelite-type molybdenum mineral) is identified at 8.6%. This mineralogical profile indicates an oxidized nature for both the molybdenum-bearing and siliceous phases. The presence of $PbMoO_4$, a partially soluble compound, suggests that molybdenum can be efficiently extracted using acid leaching. Tungsten, identified earlier as WO_3 in trace amounts (1.1%), would require more aggressive conditions, such as autoclave acid leaching. Due to the high silica content, this ore is classified as quartz-rich and may necessitate the use of hydrofluoric acid (HF) to disrupt the siliceous matrix. Therefore, Sample O-1 is considered promising for integrated Mo and W recovery using appropriately selected decomposition methods.

The diffractogram of Sample O-2 indicates the presence of two major mineral phases: $CaWO_4$ (scheelite, 59.2%) and $CaCO_3$ (calcite, 40.8%). The absence of a complex silicate matrix simplifies sample decomposition; however, scheelite itself is highly resistant to conventional acid leaching. Effective extraction of tungsten thus requires autoclave processing using acidic media with fluoride additives (*e.g.*, HF). While DFGSD calcite is readily soluble in acid, facilitating structural breakdown, the possible presence of sulfide phases such as $CuFeS_2$-though not explicitly detected may complicate leaching behavior. Overall, Sample O-2 is a high-grade scheelite ore suitable for autoclave acid leaching to recover tungsten.

Sample O-3 exhibits high mineralogical complexity, with multiple identified phases: SiO_2 (22.0%), WS_2 (tungsten disulfide, 0.9%), $NaAlSi_3O_8$ (albite, 20.3%), and $KAlSi_3O_8$ (orthoclase, 29.4%). The dominant presence of aluminosilicates forms a highly resistant mineral matrix. WS_2 represents a reduced tungsten form that is poorly soluble under standard acidic conditions, especially in open-system digestion. These characteristics classify the ore as refractory, necessitating intensive decomposition techniques such as soda sintering or autoclave treatment with HF. The quartz and feldspar components act as barriers, preventing reagents from accessing target elements. The absence of Mo-bearing phases may be attributed to either the very low molybdenum content or its occurrence in amorphous or nano-dispersed forms that are undetectable by XRD.

The XRD results for Sample O-4 show it to be predominantly composed of quartz (SiO_2 – 91.7%), with minor phases of $CaMoO_4$ (3.6%) and Fe_2O_3 (4.7%). This combination suggests that molybdenum is present in an oxidized, relatively accessible form ($CaMoO_4$), although its low concentration necessitates preliminary enrichment prior to processing. Similar to Sample O-1, the high silica content implies that aggressive treatments using HF or thermal decomposition methods are required to disrupt the matrix. The presence of iron oxides may interfere with accurate elemental analysis and thus necessitates an additional purification step-such as selective precipitation with ammonia. Overall, Sample O-4 can be classified as a low-grade, refractory ore, for which comprehensive decomposition strategies are required to enable effective Mo recovery.

In summary, the chemical and mineralogical analysis of the ore samples revealed significant variability in the composition and distribution of Mo and W phases, ranging from easily leachable oxidized compounds to highly refractory silicates and sulfides. This diversity necessitates the application of tailored decomposition strategies, considering not only the solubility of target minerals but also the structural and chemical complexity of the host matrix. These findings provide a crucial foundation for selecting and evaluating the efficiency of various sample decomposition techniques, as discussed in the following section.

3.2 Analysis of ore decomposition methods

Various decomposition methods were applied for sample preparation prior to molybdenum and tungsten content determination. The choice of method was based on the mineralogical and chemical characteristics established through XRD and XRF, as well as reference data from standard materials.

The wet decomposition method using a mixture of hydrochloric acid and hydrogen peroxide (HCl + H_2O_2, 3:1) was employed for samples O-1 and O-4, which primarily consist of quartz and silicate phases and contain trace amounts of Mo and W, mainly in the forms of $PbMoO_4$ and $CaMoO_4$. These Mo-bearing minerals, categorized as partially soluble, can be effectively dissolved due to the oxidative action of hydrogen peroxide in an acidic medium. Additionally, using ammonia as a selective precipitant for iron and other interfering species improved the accuracy of subsequent analytical determinations.

The wet method using nitric acid (HNO_3) and hydrochloric acid (HCl) was applied to samples with low content of refractory phases, such as weakly mineralized silicate rocks. This method facilitates the dissolution of carbonates, sulfides, and labile oxides. Although it provides selective decomposition of readily accessible compounds, it does not fully decompose refractory tungsten and molybdenum phases, a limitation considered when selecting subsequent methods.

Dry decomposition methods, including sintering with sodium carbonate, were used for samples O-2 and O-3, which contain highly stable mineral phases such as $CaWO_4$ (scheelite), WS_2 (tungstenite), feldspars, and quartz. XRD data indicated significant concentrations of these minerals, which exhibit low solubility in conventional acidic media. High-temperature sintering followed by acid dissolution enables efficient breakdown of the crystal lattice and conversion of W and Mo into soluble forms suitable for quantitative analysis.

Autoclave decomposition methods were applied to all sample types to intensify dissolution through elevated temperature and pressure. Autoclave digestion with nitric acid and hydrogen peroxide proved particularly effective for samples containing dispersed Mo phases (*e.g.*, MoS_2) due to the oxidation of sulfide species. Autoclaving with ammonium hydroxide allowed for removal of interfering Fe(III) and stabilization of the solution for analysis. Special emphasis was placed on autoclave decomposition with nitric and hydrofluoric acids for quartz-rich samples, where conventional methods are ineffective. The use of HF ensures the breakdown of quartz and complete release of target elements.

In summary, the combined application of acid, dry, and autoclave decomposition methods matched the mineralogical characteristics of the samples and provided the necessary degree of dissolution. This is critical for precise and reproducible determination of tungsten and molybdenum content in complex mineral matrices. Following decomposition, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to quantify Mo and W concentrations. All experiments were conducted three times, yielding a standard deviation of 3-5%. The results, recalculated from µg/L to percentages, are presented in Table 3.

According to XRD analysis, the first sample O-1 is predominantly composed of quartz (SiO_2 − 95.5%), while molybdenum and tungsten are present in sparingly soluble forms – $PbMoO_4$ and WO_3. The high quartz content results in low availability of the target components, as confirmed by the decomposition outcomes. The wet decomposition method using HCl + H_2O_2 (Method 1) yielded poor recovery of both Mo and W, which can be attributed to the chemical inertness of the quartz matrix and the insufficient reactivity of the reagents to break down $PbMoO_4$. The use of simple acids such as HCl or HNO_3 (Methods 2 and 3) resulted in partial dissolution of molybdenum but was ineffective for tungsten extraction, as WO_3 remains insoluble without prior matrix disruption. Autoclave decomposition with HNO_3 + H_2O_2 (Method 6) moderately improved Mo recovery through oxidative action; however, the overall efficiency remained limited. The most effective result was achieved using autoclave decomposition with HNO_3 + HF (Method 8), where HF significantly disrupted the siliceous matrix, promoting the transfer of Mo and, to some extent, W into solution. For this quartz-rich ore with finely dispersed molybdenum,

Table 3: Molybdenum and tungsten contents in solutions after decomposition.

№ Method	O-1		O-2		O-3		O-4	
	Mo, 10^{-3}%	W, 10^{-3}%	Mo, 10^{-3}%	W, 10^{-3}%	Mo, 10^{-3}%	W, 10^{-3}%	Mo, 10^{-3}%	W, 10^{-3}%
1	0.0655	0.0342	–	–	0.5282	0.0043	0.0024	0.0125
2	0.1974	0.0024	–	2.2927	1.1187	0.0061	–	–
3	0.0816	–	–	2.0138	0.8162	–	–	–
4	–	–	–	–	–	–	–	0.9047
5	–	–	–	–	–	–	–	0.5058
6	0.1668	–	–	0.2677	1.1177	0.0557	–	–
7	0.0350	0.0580	–	–	–	–	–	0.0142
8	0.2525	0.0255	–	3.7079	0.8715	0.1423	–	0.0288
9	–	–	–	0.1805	–	–	0.1005	–

autoclave treatment with HF proved optimal, enabling the breakdown of the resistant matrix and facilitating molybdenum solubilization. Complete tungsten recovery was not achieved, likely due to its presence in highly refractory phases.

The second sample O-2, as confirmed by the XRD results, represents a high-grade scheelite ore dominated by $CaWO_4$(59.2%) and associated calcite ($CaCO_3$ − 40.8%). This mineral composition imparts resistance to acid attack in tungsten phases, while calcite remains relatively accessible. Treatments using HNO_3 and HCl (Methods 2 and 3) achieved high tungsten recovery due to partial dissolution of calcite and subsequent breakdown of the scheelite structure. Autoclave decomposition with HNO_3 + H_2O_2 (Method 6) enhanced Mo recovery via oxidative dissolution. Although autoclave decomposition with HNO_3 + HF (Method 8) maximized Mo extraction, tungsten recovery was somewhat lower, possibly due to partial HF reaction with calcite and pH shifts affecting solution chemistry. For scheelite concentrates, classical acid leaching with HNO_3 or HCl in an open system remains the most effective approach for tungsten extraction. For complete Mo recovery, however, the use of autoclave treatment with HF is advisable.

The third sample O-3, based on the results of XRD, is characterized by a complex silicate matrix composed mainly of feldspars (albite, orthoclase), quartz, and tungsten disulfide (WS_2). This description is also confirmed by the results of the X-ray fluorescence analysis, which indicates that the macroelements in the composition of the ore are silicon, potassium, sodium, aluminum, and oxygen. This mineralogical profile imparts high resistance to decomposition and low accessibility of target elements. Wet methods (Methods 1-3) yielded only partial Mo extraction and were largely ineffective for tungsten due to the stability of the silicate matrix. Autoclave treatment with HNO_3 + H_2O_2 (Method 6) enhanced the extraction of Mo and, to a lesser extent, W, owing to intensified oxidative action at elevated temperatures. The most effective decomposition was achieved with HF−containing autoclave treatment (Method 8), which disrupted the quartz-silicate framework and released both Mo and W into solution. For silicate granitoid-type ores, autoclave treatment with HNO_3 + HF is essential to ensure efficient matrix decomposition and subsequent solubilization of the target elements.

The fourth sample O-4, based on the results of XRD is mainly composed of quartz and iron-bearing phases, with molybdenum occurring in low concentrations as $CaMoO_4$. Data from X-ray fluorescence analysis also confirms the presence of silicon, iron, calcium, and oxygen. Molybdenum was not detected by this method, possibly due to the method's sensitivity limitations. Such composition severely limits the efficiency of standard decomposition methods. Wet digestion methods demonstrated extremely poor recovery of both Mo and W due to the resistance of quartz and the low content of target minerals. Dry decomposition via sintering (Methods 4 and 5) facilitated matrix breakdown and partial W transfer to solution, highlighting the necessity of high-temperature treatment for such ores. Autoclave methods involving NH_4OH and HF (Methods 7 and 8) showed negligible extraction efficiency, reflecting the low content of Mo and W and the refractory nature of the silicate matrix. Autoclave decomposition using HCl (Method 9) led to partial Mo recovery but was insufficient for complete mineral breakdown. For ores dominated by quartz and iron-bearing phases, maximum recovery is achieved through preliminary sintering followed by acid leaching. Other methods prove largely ineffective due to the resilient mineral matrix and low concentration of Mo and W.

Depending on the mineralogical composition of the ores, different decomposition strategies demonstrated optimal performance: quartz-silicate and granitoid ores required autoclave methods involving HF or high-temperature sintering; scheelite concentrates responded well to conventional acid leaching without the use of hydrofluoric acid; and low-grade or refractory ores necessitated more aggressive decomposition regimes to disrupt the matrix structure.

Our research, from the perspective of sustainable development, demonstrates that improving decomposition technologies brings both environmental and economic benefits. Autoclave decomposition, carried out at temperatures of 75-175 °C for 20-35 minutes, significantly reduces energy consumption compared to the traditional sintering method (900-950 °C for 2 hours). HF technology is applied to quartz-containing ores that are difficult to decompose and is implemented in a sealed autoclave system. The microwave digestion system significantly reduces the risks of emissions and eliminates the need for direct operator intervention when compared to conventional open-system methods for converting ore into solution. Optimization of ore processing protocols for a specific type of ore allows minimizing reagent consumption. For example, for scheelite concentrates, simple acid leaching (HNO_3 or HCl) is sufficient, while more aggressive methods, such as sintering with Na_2CO_3 or HF treatment are required for ores with increased resistance. In addition, selective methods, such as autoclave or acid decomposition, generate less alkaline waste compared to mass sintering, which has a positive effect on the operation of recycling systems. Thus, the presented approach not only

Table 4: Comparative analysis of decomposition conditions reported in the literature and those used in this study.

Method	Reagents/Fluxes	Parameters	Time, min	Features	Reference
Two-stage acid decomposition	HCl, HNO_3, HF	80-90 °C	60-240	Selective dissolution of Mo and W	[11]
Autoclave alkaline treatment	NaOH	80-160 °C	60-120	For scheelite ($CaWO_4$)	[12]
Solvometallurgical leaching with NASX (non-aqueous solvent extraction)	Mixture of 2 M HCl and ethylene glycol (EG) for scheelite dissolution Extractant: 20% Aliquat 336 in GS190 + 10% 1-decanol Precipitation: NH_3 + NH_4Cl	60 °C	>240	Mild and environmentally friendly method	[10]
Microwave−assisted decomposition	HNO_3, HCl, HF, $C_6H_8O_7$	270-280 °C, 4-5 MPa	40-60	Rapid, compatible with ICP-MS	[26]
Conventional acid and alkaline sintering	HCl, Na_2CO_3, NaOH	540 °C	–	Conventional method	[15]
Acid leaching and extraction	H_2SO_4	95 °C	120	Objective – decomposition of scheelite ($CaWO_4$), achieving W recovery up to 99.8% and Mo up to 98%	[31]
Extraction following oxidation	H_2O_2 + TBP/TRPO	<50 °C	–	Dissolution of W as peroxotungstate, extraction of Mo	[32]
Sintering followed by HCl leaching	Na_2CO_3	750–850 °C	45–60	Applied sulfide reduction, W recovery ~90%	[33]
Sintering with K_2CO_3 followed by acid treatment	K_2CO_3 + HCl	800–850 °C	100–120	Comparison of K_2CO_3 and Na_2CO_3; focus on low-grade wolframite	[34]
Dissolution using three different approaches	HCl, HNO_3, HF, H_2O_2, NH_4 OH, Na_2CO_3	80 °C (acid leaching) 900-950 °C (sintering) 80-175 °C (autoclave treatment)	10−120	Four ore types tested for the first time, direct process scheme comparison	This work

increases the efficiency of Mo and W extraction but also demonstrates quantifiable advantages in terms of sustainability.

To assess the reliability of the chosen decomposition strategies in the context of established research, a comparative review of approaches applied by other authors was conducted (Table 4). This table summarizes key parameters (temperature, reagents, pressure, duration) and decomposition characteristics used in other studies, highlighting their differences from the methods applied in the present work. This comparison allows for a more precise evaluation of the advantages and limitations of various approaches for processing tungsten-molybdenum ores. Leaching methods often prioritize highly aggressive chemical environments, particularly for refractory ores. For example, a conventional approach for scheelite and silicate-rich matrices involves sintering with Na_2CO_3 at temperatures

exceeding 900°C, followed by acid leaching. However, this method is energy-intensive and may introduce additional operational challenges. By contrast, autoclave methods employing HNO_3-HF or HCl under pressure offer more selective decomposition of quartz and tungstate matrices with significantly reduced energy input, as also demonstrated in the current study.

Several literature methods employ fluorides (*e.g.*, HF or NaF) to target silicate breakdown and facilitate the release of tungsten and molybdenum. While effective, fluoride handling presents environmental and safety concerns. In this study, careful control of HF concentration within a closed autoclave system achieved high recovery rates while mitigating exposure risks.

Furthermore, many prior studies do not address natural ore variability, often using synthetic or high-grade single-mineral standards. In contrast, the present work accounts for real-world geological complexity by examining four ore types with diverse mineralogical profiles, including low−grade and refractory varieties and applies nine decomposition strategies. This broad approach enhances the robustness and practical relevance of the findings.

As shown by the comparative analysis, the methods applied in this study, especially autoclave decomposition using nitric and hydrofluoric acids, provide comparable or even higher dissolution efficiency for complex molybdenum and tungsten ores compared to previously reported approaches. While many of those approaches focus on specific ore types or rely on single-stage decomposition, our integrated methodology is suitable for a wide range of mineral matrices, including quartz-containing, silicate, and refractory scheelite ores. The findings emphasize the importance of adjusting decomposition conditions to the mineralogical composition of the ore and demonstrate the practical benefits of combining acid treatment, autoclaving, and sintering techniques in both analytical and industrial applications.

4. Conclusion

The research conducted demonstrated that the efficiency of molybdenum and tungsten recovery from various ore types is directly influenced by both the mineral composition and the selected decomposition strategy. In particular, for ores with high quartz content and stable molybdenum and tungsten phases, conventional acid-based methods proved insufficient due to the low solubility of the target elements. The highest molybdenum recovery rates were achieved using an autoclave method involving a combination of nitric and hydrofluoric acids (HNO_3 + HF), owing to HF's ability to effectively break down siliceous and feldspathic matrices and release Mo-bearing compounds, as evidenced in samples O-1 ($0.25\cdot 10^{-3}$%) and O-3 ($0.87\cdot 10^{-3}$%). For scheelite concentrates (O-2), the optimal approach involved classical acid leaching with either HNO_3 ($2.29\cdot 10^{-3}$%) or HCl ($2.01\cdot 10^{-3}$%) in an open system. This facilitated high tungsten yields due to the dissolution of calcite and structural transformation of scheelite. However, complete release of molybdenum-even from relatively enriched concentrates was only feasible under autoclave conditions involving HF. For natural samples O-3 and O-4, which exhibit complex chemical compositions and fall under the category of refractory siliceous Mo-W ores, the extraction efficiencies were significantly lower. This confirms the necessity of more aggressive processing strategies. The best recovery rates achieved were $0.87\cdot 10^{-3}$% Mo and $0.14\cdot 10^{-3}$% W for sample O-3, and $0.10\cdot 10^{-3}$% Mo and $0.90\cdot 10^{-3}$% W for sample O-4. These results highlight the limitations of standard techniques and support the use of autoclave schemes incorporating hydrofluoric acid or prior sintering to disrupt the stable siliceous matrix. The practical significance of this study lies in the demonstrated effectiveness of autoclave methods involving hydrofluoric acid for refractory quartz and granitoid ores. These methods enable the destruction of siliceous matrices, promote more complete molybdenum recovery, and facilitate partial tungsten dissolution. For scheelite concentrates, classical acid leaching with nitric or hydrochloric acid is economically viable, offering efficient tungsten extraction without the use of fluoride reagents, thereby reducing both environmental impact and operational expenses. In the case of quartz-iron ores with low target element content, sintering followed by acid decomposition remains the preferred approach for breaking down resistant phases and converting a portion of the metals into soluble forms. This study employed an integrated approach to optimize decomposition conditions, incorporating traditional wet methods (HCl + H_2O_2, HNO_3, HCl), dry sintering with subsequent acid leaching, and autoclave techniques using various reagent systems. Unlike conventional schemes, the proposed methods offer a balance of processability and efficiency: oxidative mixtures accelerate decomposition, sintering breaks down resistant mineral structures, and autoclave digestion with HNO_3, H_2O_2, and HF maximizes molybdenum recovery without the need for complex multistage equipment. This adaptability to the specific mineralogy of the ore, including natural deposits from Central Kazakhstan, enhances the efficiency of integrated recovery of valuable components. A tailored, case-specific approach to the selection of ore processing techniques significantly improves the recovery rates of molybdenum and tungsten and enhances the overall efficiency of the

technological process.

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Conflict of Interest

There are no conflicts to declare.

Supporting Information

Not applicable.

CRediT Statement

Akmaral Ismailova: Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – Review & editing. **Dilyara Rashit:** Conceptualization, Data curation, Investigation, Visualization, Writing – Original draft. **Elena Zlobina:** Methodology, Software, Validation. **Elnura Amanova:** Investigation, Formal analysis. **Yerbol Tileuberdi:** Software, Validation, Writing – Review & editing.

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