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Potential–pH Analysis of Selective Separation Conditions of Dysprosium, Molybdenum, and Tellurium Metals from Technogenic Solutions

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Abstract— *This study evaluates the thermodynamic feasibility of selectively extracting rare metals such as dysprosium (Dy), molybdenum (Mo), and tellurium (Te) from technogenic solutions formed during the scrubbing of process gases at the Almalyk MMC Copper Smelting Plant. Potential–pH (E–pH) diagrams for each metal were generated using the FactSage software to identify the stable phases. The analyses demonstrated that Dy can be precipitated as* Dy_2O_3 *under alkaline conditions (pH > 7.5), Te as* TeO_2 *under oxidizing-neutral conditions (pH 5–8, E = 0.5–0.7 V), and Mo as* MoO_2 *in the pH range of 5–9 (E = 0.0–0.5 V). The characteristics of the precipitated phases and the influence of competing ions were examined to determine optimal conditions for selective separation. In particular, it was shown that the selectivity of Dy can be enhanced using masking agents (e.g., EDTA, citrate), Te can be recovered in the initial stage by controlling the oxidation potential, and Mo can be precipitated selectively against the background of other metals by exploiting phase distinctions. The findings of this research contribute significantly to the efficient recovery of economically valuable components from technogenic solutions and to the development of waste-free technologies.*

Keywords: technogenic solutions, rare metals, selective precipitation, potential–pH diagram, thermodynamic analysis, FactSage software, utilization of secondary resources.

1. INTRODUCTION

Technological gases generated during copper production typically contain high concentrations of sulfur-bearing components—primarily sulfur dioxide (SO_2) and sulfur trioxide (SO_3) [1]. To prevent environmental pollution and ensure the economically efficient processing of these gases, they are commonly utilized in the production of sulfuric acid (H_2SO_4). One of the crucial stages in this process is the initial scrubbing of the gases with water, which results in the formation of a process solution containing dust particles as well as dissolved SO_2 and SO_3 [2].

Although such technogenic solutions are primarily regarded as sources of acidity, they may also contain various concentrations of heavy metals, rare elements, and even precious metals. Elements such as silver (Ag), antimony (Sb), tellurium (Te), dysprosium (Dy), and others can transition into the gas phase during pyrometallurgical processing, smelting, and refining of copper concentrates, and subsequently condense into the aqueous phase during scrubbing [3]. Therefore, instead of treating these solutions as mere waste, it is of significant interest to explore the potential for recovering economically valuable components from them [4].

The extraction of valuable and rare metals from technogenic solutions formed during gas scrubbing not only enhances the efficiency of utilizing secondary resources, but also contributes to environmental safety and facilitates the transition of industrial operations toward zero-waste production. This study focuses on analyzing the composition of such solutions and developing and evaluating technologies for recovering economically significant components from them [5].

2. MATERIALS

The primary object of this study was the technogenic solutions obtained from the scrubbing of process gases emitted from smelting furnaces at the Copper Smelting Plant of Almalyk Mining and Metallurgical Complex (AMMC). One of the representative samples of such a solution was subjected to chemical analysis, and its composition is presented in Table 1.

Based on the data in Table 1, the elements with the highest concentrations are tin (Sn – 205.32 mg/L), sulfur (S – 142.49 mg/L), chlorine (Cl – 119.47 mg/L), dysprosium (Dy – 112.39 mg/L), and tellurium (Te – 92.04 mg/L). The concentrations of heavy metals such as lead (Pb), iron (Fe), copper (Cu), and zinc (Zn) are relatively low (around or below 20 mg/L), which corresponds to the nearly transparent appearance of the solution. Among the rare earth elements, dysprosium (Dy) is notably high at 112.39 mg/L, indicating a strong correlation with process gases. Microcomponents such as arsenic (As), antimony (Sb), silver (Ag), and molybdenum (Mo) are also present, with concentrations ranging from 2 to 16 mg/L.

3. RESEARCH METHODOLOGY

To investigate the chemical composition of the solutions in detail, modern analytical techniques were employed, including atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography, and other laboratory methods. The effectiveness of various separation technologies such as chemical precipitation, extraction, ion exchange, and membrane-based separation was assessed for the recovery of the identified elements [6]. The results demonstrated that these technogenic solutions should not be regarded as simple waste, but rather as secondary resources with significant economic value.

Table 1: Chemical composition of the technogenic solution (mg/L)

№	Element	Concentration (mg/L)
2	Sn	205,32
3	S	142,49
4	Cl	119,47
5	Dy	112,39
6	Te	92,04
7	Ni	70,80
8	Pb	21,77
9	Fe	18,67
10	Cu	17,88
11	Zn	17,79
12	Br	16,99
13	Sb	16,55
14	Ag	12,04
17	As	4,27
18	Mo	2,58

Thus, the extraction of rare and valuable metals from the solutions generated during the utilization of process gases contributes not only to the realization of zero-waste production but also to enhanced environmental safety and more efficient use of available resources.

The solutions obtained from gas scrubbing contain various ions, including precious metals (Ag), metalloids (Sb, Te), and rare metals (Dy), each of which transitions into a stable phase or forms a precipitate under specific conditions of pH and electrochemical potential. Therefore, constructing potential–pH (E–pH) diagrams for these components is of both practical and theoretical significance in achieving efficient separation.

E–pH diagrams (also known as Pourbaix diagrams) reflect the thermodynamic stability of a given element in an aqueous medium. Based on these diagrams, it is possible to determine the conditions under which ions in the solution exist as dissolved species, solid precipitates (e.g., oxides, hydroxides, sulfides), or in their elemental form. This information is crucial for monitoring and controlling selective separation and precipitation processes [7].

Since several metal ions coexist simultaneously in technological solutions, it is essential to determine the optimal pH and electrode potential values while accounting for their mutual chemical interactions. In particular, ions such as Ag^{+}, Sb^{3+}, and Te^{4+} can form different oxidation states under the influence of inorganic acids or oxidizing environments. Therefore, for these metals, the precipitation boundaries must be clearly defined using E–pH diagrams [8].

Furthermore, these diagrams play a vital role in ensuring the environmental and technological safety of the separation process, as incorrect pH or potential conditions may lead to the formation of hazardous compounds (e.g., volatile hydrides, soluble complex ions). E–pH diagrams help to prevent such undesirable outcomes.

In summary, constructing potential–pH diagrams are essential and highly relevant for the scientific planning of efficient and selective precipitation of valuable and rare metals from technogenic solutions, as well as for the development of recovery technologies.

In this study, the FactSage 8.2 software package was used to construct the potential–pH (E–pH) diagrams for the metals Dy, Mo, and Te. FactSage is a modern computational platform with a thermodynamic database and automated phase diagram generation capabilities, widely used in metallurgy, chemistry, and materials science [9].

4. RESULTS AND DISCUSSION

In developing selective extraction technologies for rare metals from technological solutions, it is essential to thoroughly investigate their thermodynamic stability characteristics in aqueous environments. In particular, metals such as dysprosium (Dy), molybdenum (Mo), and tellurium (Te) can exist in various oxidation states and phases—either as dissolved ions or solid precipitates—depending on the solution conditions. Accurately predicting the specific conditions (i.e., defined pH and electrode potential (E) values) under which these metals transition into stable phases allows for the scientific optimization of selective precipitation processes.

The construction of E–pH (potential–pH) diagrams was based on the following parameters:

1. System: Metal–H_2O at 298.15 K (25°C);
2. Activity: 1 mol/kg (standard concentration);
3. Closed environment: 1 atm pressure, with standard partial pressures for O_2 and H_2 gases.

The primary objective of constructing potential–pH diagrams for the rare metals in solution was to determine the stability domains of each metal in its ionic, oxide, hydroxide, or elemental forms within an aqueous medium.

For each metal, the stable phases—such as Dy^{3+} / $Dy_2O_3(s)$, MoO_4^{2-} / $MoO_2(s)$, $Te(OH)_6^{2-}$ / $TeO_2(s)$ / Te(s), and others—were identified and represented graphically as functions of pH and electrode potential. These diagrams enabled the prediction of conditions under which individual components could be selectively separated, even in the presence of other metals in the solution.

The use of the FactSage software package made it possible to model the behavior of metals within complex redox systems from a thermodynamic perspective. In particular, the accurate determination of E–pH boundaries and stability zones for selective precipitation proved to be a critical factor in optimizing the technological process.

Thus, the E–pH diagrams constructed in this study for Dy, Mo, and Te (Figures 1, 2, and 3) served as a key tool in developing a scientifically grounded strategy for the selective recovery of these rare metals from technogenic solutions.

The Pourbaix diagram for molybdenum present in the solution is shown in Figure 1.

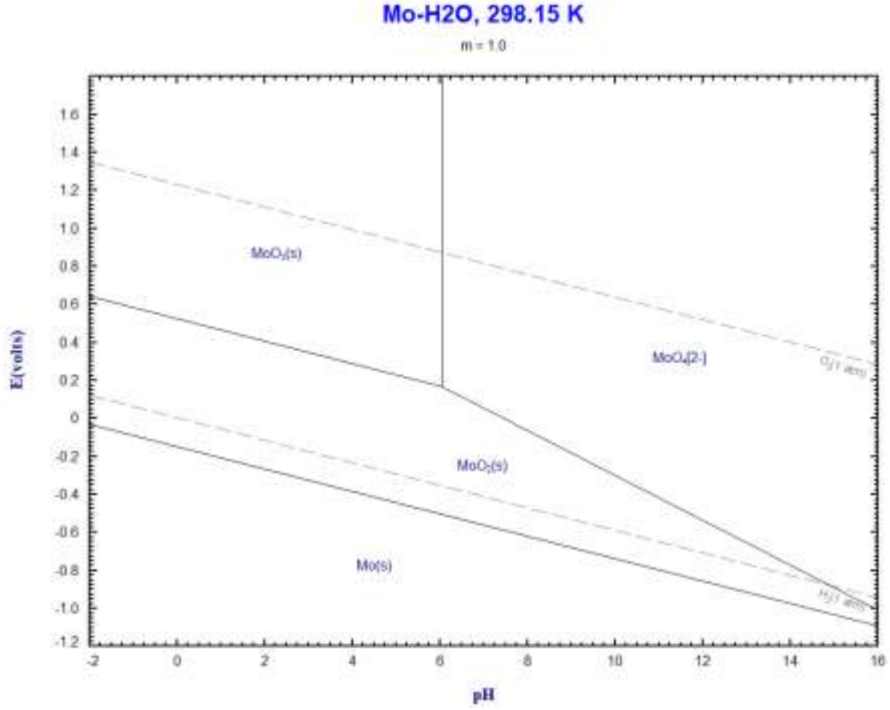

Fig. 1. *Pourbaix Diagram for the Mo–H_2O System*

Molybdenum (Mo) can exist in various oxidation states in technogenic solutions, and during its precipitation process, it predominantly forms solid oxide phases such as MoO_3 and MoO_2, or can be recovered in metallic form. As illustrated in Figure 1, based on thermodynamically stable phase regions, $MoO_3(s)$ is expected to precipitate under acidic conditions with a pH range of approximately 0–5 and an electrode potential (E) between 0.5–1.2 V. $MoO_2(s)$, on the other hand, forms under near-neutral to slightly alkaline conditions (pH 5–9) with a lower potential range of 0.0–0.5 V.

The recovery of Mo in metallic form is feasible only under strongly reducing conditions, specifically at pH values above 9 and electrode potentials below –0.2 V. From a practical and operational standpoint, the most efficient and stable method for Mo separation is its precipitation as $MoO_2(s)$ in a neutral medium (pH 5–9) at around 0 V, which ensures both selectivity and process stability.

Dysprosium (Dy) is present in technogenic solutions primarily in the form of Dy^{3+} ions, which readily precipitate as $Dy_2O_3(s)$ under alkaline conditions. Thermodynamic analysis indicates that stable precipitation of Dy occurs at pH values greater than 7.5, while the electrode potential has negligible influence on this process (Figure 2). Therefore, to effectively separate Dy from solution, the pH should be increased to the range of 8–10, which can be achieved by adding alkaline agents such as NaOH or NH_4OH.

Under these conditions, Dy can be selectively recovered in the form of $Dy_2O_3(s)$, while other metals such as Mo and Te remain in dissolved form and do not precipitate. This pH-controlled separation ensures the selective recovery of dysprosium with minimal interference from coexisting elements.

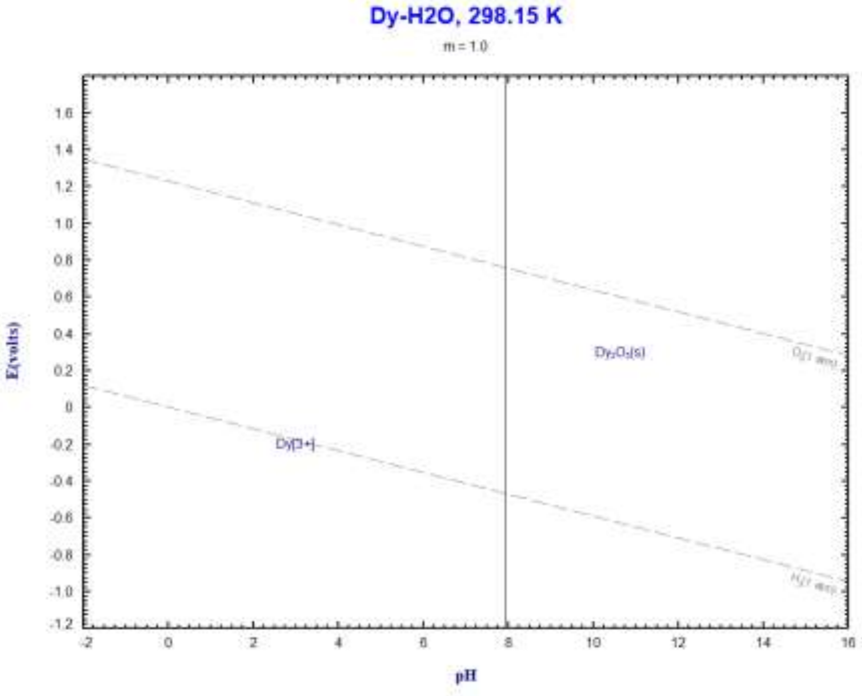

Fig. 2. *Pourbaix Diagram for the Dy–H_2O System*

Tellurium (Te) is predominantly present in technogenic solutions in oxidized forms, such as Te^{4+} or Te(VI) ions. For selective recovery, electrochemical conditions in the range of pH 5–8 and electrode potentials between 0.5–0.7 V are considered optimal (Figure 3). Under these conditions, $TeO_2(s)$ is formed as a thermodynamically stable precipitate. The desired potential can be maintained by introducing mild oxidizing agents such as H_2O_2 into the solution.

The formation of $TeO_2(s)$ near neutral pH conditions enables sequential separation of Te from other metals such as Dy and Mo. Thus, the stepwise adjustment of both pH and potential is essential for the effective and selective precipitation of each element, allowing the development of a comprehensive strategy for the sequential recovery of Dy, Te, and Mo from solution.

4.1. ANALYTICAL EVALUATION OF SELECTIVE RECOVERY POTENTIAL FOR RARE METALS FROM SOLUTION

The potential for selective recovery of dysprosium (Dy) from technogenic solutions demonstrates that Dy^{3+} ions form a stable Dy_2O_3 precipitate only under alkaline conditions, specifically at $pH > 7.5$. However, in such conditions, other metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+}, and Fe^{3+} may also form their respective hydroxide precipitates. This co-precipitation effect complicates the selective separation of Dy in the presence of these competing heavy metal ions.

An analytical approach suggests that within the pH range of 8–9, partial precipitation of these heavy metals may occur concurrently with Dy. To enhance selectivity, pre-extraction or the use of masking agents such as EDTA or citric acid is recommended. These chelating agents form stable complexes with heavy metals, retaining them in dissolved form and preventing their precipitation. Consequently, Dy^{3+} ions can be selectively precipitated as Dy_2O_3, enabling more efficient separation from coexisting ions.

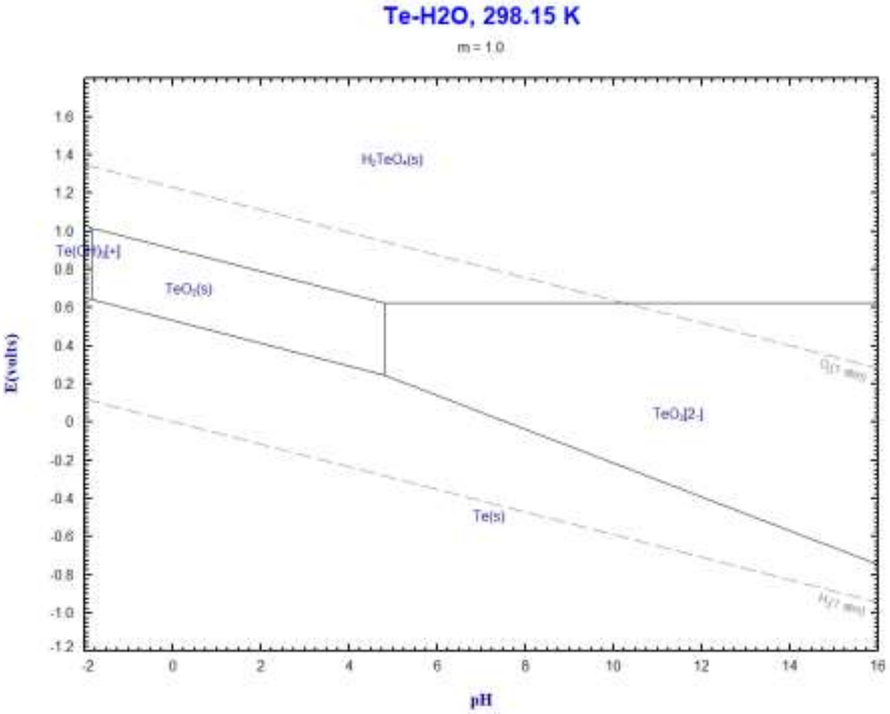

Fig. 3. *Pourbaix Diagram for the Te–H_2O System*

In the case of tellurium (Te), selective recovery from solution occurs primarily through the formation of TeO_2 precipitate under mildly oxidizing conditions, specifically within pH 5–8 and an electrode potential of 0.5–0.7 V. However, under such redox conditions, other ions such as Sn(IV), Sb(III), Fe(III), and Ag(I) may also exist in forms prone to precipitation. These competing species pose challenges for Te selectivity.

To overcome this, a stepwise separation strategy based on differences in redox potentials can be applied. Research shows that the stable phase of TeO_2 forms at lower potentials than that of silver and antimony oxides. Therefore, by carefully controlling the oxidizing strength of the solution—especially by adjusting the dosage of oxidizing agents like H_2O_2—tellurium can be selectively precipitated before other metal ions begin to form solids. This approach enhances the efficiency and selectivity of Te recovery and facilitates subsequent separation steps for other metals.

Molybdenum (Mo), typically present in technogenic solutions as Mo^{6+} ions, precipitates as MoO_2 under conditions of pH 5–9 and electrode potentials between 0.0–0.5 V. However, in this pH range, other heavy metals such as iron (Fe), zinc (Zn), and lead (Pb) are also capable of forming hydroxide precipitates. This overlap introduces challenges for selective Mo separation.

Nonetheless, the phase distinction—where Mo forms an oxide precipitate and other metals form hydroxides—can be strategically exploited for selective separation. Utilizing this difference, MoO_2 can be isolated from solution while minimizing interference from co-precipitating hydroxides. As a result, molybdenum can be efficiently recovered under controlled conditions with minimal influence from other metal species.

5. CONCLUSION

The results of this study demonstrate that technogenic solutions derived from copper smelting processes contain rare metals such as Dy, Mo, and Te, which can be selectively recovered based on scientifically grounded methods. For each element, optimal precipitation conditions were identified using potential–pH (Pourbaix) diagrams, allowing for the determination of technologically applicable pH ranges and electrochemical potentials.

It was confirmed that dysprosium can be selectively precipitated as Dy_2O_3 at pH > 7.5, tellurium as TeO_2 within the pH range of 5–8 and electrode potential of 0.5–0.7 V, and molybdenum as MoO_2 at pH 5–9 and 0.0–0.5 V. However, the presence of other heavy metals (such as Fe, Zn, Cu, Ag, Sb, etc.) in the solution may introduce ion competition, hindering selectivity.

To enhance the efficiency of selective separation, several approaches are recommended, including the use of masking agents, control of the oxidizing environment, and application of filtration technologies based on differences in the physical nature of the resulting precipitates.

Ultimately, in-depth analysis and recovery of rare metals from technogenic solutions present a promising opportunity to increase the utilization of secondary raw material sources, facilitate the transition toward zero-waste technologies, and improve environmental safety.

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