

Thermodynamic analysis of Mn-As-H₂O, Mn-Sb-H₂O, Mn-Bi-H₂O systems

Khylysh Beisenovich Omarov, Saule Kidirbaevna Aldabergenova, Zaure Bakikyzy Absat, Nazym Zhanbyrbaevna Rakhimzhanova, Asel Berikovna Siyazova

Abstract—A thermodynamic analysis of Mn-As-H₂O, Mn-Sb-H₂O, Mn-Bi-H₂O systems was made through calculation and drawing diagrams of E-pH, where the boundaries of the area of sustainability and formation of arsenates, antimonates and bismuthates of manganese are clearly shown.

Keywords— Antimony, arsenic, bismuth, diagram of the E-pH.

I. INTRODUCTION

IN the production of nonferrous metals, arsenic, antimony and bismuth are harmful impurities. During copper electrolysis, their transition from anode copper to solution and contamination of the electrolyte are happening. The accumulation of significant quantities of harmful impurities in the electrolyte may cause a resistance increase, the solution viscosity, resulting in over-expenditure of electricity, which poses the problem of the withdrawal from circulation and purification of electrolyte copper-melting production.

In world practice, different techniques are used for these purposes, their analysis shows that there is still a question of purifying electrolyte, because applied methods do not allow to reach a deep degree of solutions cleaning. Arsenic, antimony-, and bismuth compounds circulate in many metallurgical processes of nonferrous metallurgy, complicating the course of technological processes, thereby reducing their cost-effectiveness.

Development of complex processing of copper electrolyte with arsenic, antimony and bismuth exclusion in environmentally friendly forms require a preliminary thermodynamic analysis to predict the behavior of the copper electrolyte components during cleaning process.

For the purpose of theoretical justification of physical and chemical laws in process of hydrolytic deposition of arsenic, antimony and bismuth from copper electrolyte by manganese-containing compound thermodynamic analysis of Mn-As-H₂O, Mn-Sb-H₂O, Mn-Bi-H₂O systems was made.

II. MATERIALS AND METHODS

By calculating and charting E-pH diagrams, the boundaries of the area of sustainability and boundaries of formation of arsenates, antimonates and manganese bismuthates are clearly shown. Data analysis of diagrams

allowed to solve a number of issues related to the chemical reactions in the studied systems, the direction of the reactions and resistance components of the phases, to evaluate the thermodynamic behavior of the chemical elements and their compounds, to set limits on capacity and pH, in which the compound is sustainable, to identify the chemical nature of oxidation, recovery products.

Fig. 1 is a diagram of the E-pH Mn-As-H₂O system at standard conditions (25°C and a total pressure of 1 atm.), firstly built with all forms of ortho- and metaarsenic acid-pH diagrams of E-pH As-H₂O and Mn-H₂O systems. Line 1, 2 on E-pH diagram correspond to the upper (oxidizing environment) and lower (reducing environment) boundaries of water sustainability.

All equations of As-H₂O systems reactions are indicated by dash-dotted lines. The main formula in the oxidative area of arsenic in the range pH 0-2,19 is undissociated H₃AsO₄, in the pH range equal to 2,19 -6,79 - H₂AsO₄⁻, at pH values from 6.79 to 11.51 dominates HAsO₄²⁻ ion. At pH > 11.51, AsO₄³⁻ anion appears. In recovering environment, undissociated H₃AsO₃-arsenic acid, is stable, which with an increase in pH will be replaced by H₂AsO₃⁻, HAsO₃²⁻, and AsO₃³⁻. H₃AsO₃ oxidation by increasing the values of the potential lead to the formation of H₃AsO₄, H₂AsO₄⁻ or HAsO₄²⁻ ions; and H₂AsO₃⁻ can be oxidized to HAsO₄²⁻ and AsO₄³⁻ (reaction equation from 3 to 28 of Table I).

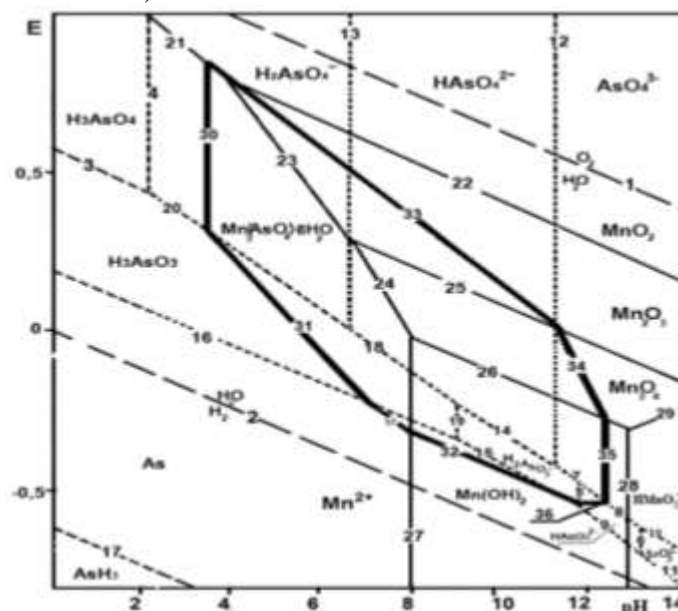


Fig. 1 E-pH system diagram Mn-As-H₂O

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TABLE I
SYSTEM INTERACTION EQUATIONS MN-AS-H₂O

N _o	Chemical reactions	Electrode reactions
1	$H_2O_{(l)}-O_{2(g)}+4H^+_{(aq)}+4e^-$	$E=1,23-0,059pH$
2	$H_{2(g)}=2H^+_{(aq)}+2e^-$	$E=-0,059pH$
3	$H_3AsO_{3(0)}+H_2O_{(l)}=H_3AsO_{4(0)}+2H^+_{(aq)}+2e^-$	$E=-0,586-0,059pH$
4	$H_3AsO_{4(0)}=H_2AsO_{4(0)}+H^+_{(aq)}$	$lgK_p=-pH; pH=2,2$
5	$H_2AsO_3^-(0)=HASO_3^-(0)+H^+_{(aq)}$	$lgK_p=-pH; pH=12,1$
6	$HAsO_3^-(0)=H^+_{(aq)}+AsO_3^-(0)$	$lgK_p=-pH; pH=13,4$
7	$H_2AsO_3^-(0)+H_2O_{(l)}=AsO_4^-(0)+4H^+_{(aq)}+2e^-$	$E=0,925-0,118pH$
8	$HAsO_3^-(0)+H_2O_{(l)}=AsO_4^-(0)+3H^+_{(aq)}+2e^-$	$E=0,567-0,088pH$
9	$As_{(s)}+3H_2O_{(l)}=HASO_3^-(0)+5H^+_{(aq)}+3e^-$	$E=0,65+0,02lg[HASO_3^-(0)]-0,1pH$
10	$AsO_3^-(0)+H_2O_{(l)}=AsO_4^-(0)+2H^+_{(aq)}+2e^-$	$E=-0,170-0,059pH$
11	$As_{(s)}+3H_2O_{(l)}=AsO_3^-(0)+6H^+_{(aq)}+3e^-$	$E=-0,892-0,118pH$
12	$HAsO_4^-(0)=H^+_{(aq)}+AsO_4^-(0)$	$lgK_p=-pH; pH=11,5$
13	$H_2AsO_4^-(0)=HASO_4^-(0)+H^+_{(aq)}$	$lgK_p=-pH; pH=6,7$
14	$H_2AsO_3^-(0)+H_2O_{(l)}=HASO_4^-(0)+3H^+_{(aq)}+2e^-$	$E=-0,585-0,088pH$
15	$As_{(s)}+3H_2O_{(l)}=H_2AsO_3^-(0)+4H^+_{(aq)}+3e^-$	$E=0,41+0,02lg[H_2AsO_3^-(0)]-0,08pH$
16	$As_{(s)}+3H_2O_{(l)}=H_3AsO_3(0)+3H^+_{(aq)}+3e^-$	$E=0,23+0,02lg[H_3AsO_3(0)]-0,06pH$
17	$AsH_{3(g)}=As_{(s)}+3H^+_{(aq)}+3e^-$	$E=-0,627-0,059pH$
18	$H_3AsO_{3(0)}+H_2O_{(l)}=HASO_4^-(0)+4H^+_{(aq)}+2e^-$	$E=-0,858-0,118pH$
19	$H_3AsO_{3(0)}=H_2AsO_3^-(0)+H^+_{(aq)}$	$lgK_p=-pH; pH=9,2$
20	$H_3AsO_{4(0)}=H_2AsO_4^-(0)+H^+_{(aq)}$	$lgK_p=-pH; pH=2,2$
21	$Mn^{2+}_{(aq)}+2H_2O_{(l)}=MnO_{2(s)}+4H^+_{(aq)}+2e^-$	$E=1,258-0,118pH$
22	$Mn_2O_{3(s)}+H_2O_{(l)}=2MnO_{2(s)}+2H^+_{(aq)}+2e^-$	$E=1,014-0,059pH$
23	$2Mn^{2+}_{(aq)}+3H_2O_{(l)}=Mn_2O_{3(s)}+6H^+_{(aq)}+2e^-$	$E=1,502-0,177pH$
24	$3Mn^{2+}_{(aq)}+4H_2O_{(l)}=Mn_3O_4(s)+8H^+_{(aq)}+2e^-$	$E=1,912-0,236pH$
25	$2Mn_3O_4(s)+H_2O_{(l)}=3Mn_2O_3(s)+2H^+_{(aq)}+2e^-$	$E=-0,689-0,059pH$
26	$3Mn(OH)_{2(s)}=Mn_3O_4(s)+2H_2O_{(l)}+2H^+_{(aq)}+2e^-$	$E=0,402-0,059pH$
27	$Mn^{2+}_{(aq)}+2H_2O_{(l)}=Mn(OH)_{2(s)}+2H^+_{(aq)}$	$lgK_p=-lg[Mn^{2+}]-2pH; pH=8$
28	$Mn(OH)_{2(s)}=HMnO_2^-(0)+H^+_{(aq)}+2e^-$	$lgK_p=lg[HMnO_2^-]-pH; pH=13$
29	$3HMnO_2^-(0)+H^+_{(aq)}=Mn_3O_4(s)+2H_2O_{(l)}+2e^-$	$E=1,317+0,295pH$
30	$3Mn^{2+}_{(aq)}+H_2AsO_4^-(0)+8H_2O_{(l)}=Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}+4H^+_{(aq)}$	$lgK_p=4-4pH; pH=3,4$
31	$3Mn^{2+}_{(aq)}+H_3AsO_{3(0)}+10H_2O_{(l)}=Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}+10H^+_{(aq)}+4e^-$	$E=0,7817$
32	$3Mn(OH)_{2(s)}+2As_{(s)}+10H_2O_{(l)}=Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}+10H^+_{(aq)}+10e^-$	$E=0,1826-0,059pH$
33	$3Mn_2O_3(s)+4HASO_4^-(0)+7H_2O_{(l)}=2Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}+2H^+_{(aq)}+10e^-$	$E=-0,904-0,0118pH$
34	$Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}=Mn_3O_4(s)+2AsO_4^-(0)+4H_2O_{(l)}+8H^+_{(aq)}+2e^-$	$E=2,59-0,236pH$
35	$3Mn(OH)_{2(s)}+2AsO_4^-(0)+2H_2O_{(l)}+6H^+_{(aq)}=Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}$	$lgK_p=-2lg[AsO_4^-(0)]+6pH; pH=12,5$
36	$Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}=3Mn(OH)_{2(s)}+2HASO_3^-(0)+4H_2O_{(l)}$	$E=-0,552$
37	$3Mn^{2+}_{(aq)}+2As_{(s)}+16H_2O_{(l)}=Mn_3(AsO_4)_2\cdot 8H_2O_{(s)}+16H^+_{(aq)}+10e^-$	$E=0,466-0,0944pH$

All reactions (from 21 to 29 in Table I) of Mn-H₂O system are indicated by solid lines, which shows the interaction and the area of existence of manganese ions: Mn²⁺, HMnO₂⁻ oxides and manganese hydroxide Mn₂O₃, Mn₃O₄, MnO₂, Mn(OH)₂. Reaction equations numbered from 30 to 37 in Table I correspond to the area of existence of manganese arsenate composition Mn₃(AsO₄)₂·8H₂O, the boundaries of which are marked by solid bold lines of manganese arsenate Mn₃(AsO₄)₂·8H₂O occupies an area of stability in the pH range from 3.45 (line 30) to 12.5 (line 35) and the value of the redox potential from -0.52 V (lines 32, 35, 36) to + 0.77 V

(line 30, 33). This composition of manganese arsenate is stable in wide range, but under standard conditions in highly acidic environment (pH <3.45) and in highly alkaline environment (pH > 12.5).

On Fig. 2, for the first time diagram of E-pH system of Mn-Sb-H₂O under standard conditions by combining private Sb-H₂O system diagram with private diagram of Mn-H₂O system is shown.

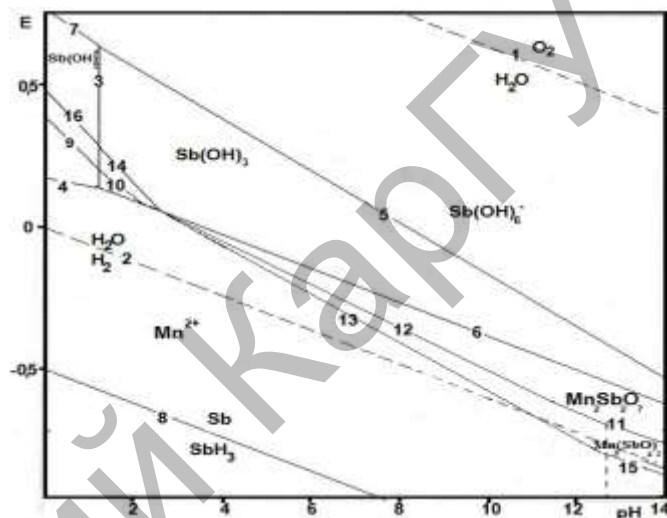


Fig. 2 Diagram of E-pH system of Mn-Sb-H₂O

The first two equations are the reactions of the upper and lower boundaries of water sustainability. The following reaction under 3 to 8 numbers of Table II correspond to all possible interactions of Sb-H₂O system, showing the interaction region and the existence of dissolved antimony: Sb(OH)₂⁺, Sb(OH)₃, Sb(OH)₆⁻, also SbH₃ and Sb⁰.

TABLE II
System interaction equations Mn-Sb-H₂O

N _o	Chemical reaction	Electrode reaction
1	$H_2O_{(l)}-O_{2(g)}+4H^+_{(aq)}+4e^-$	$E=1,23-0,059pH$
2	$H_{2(g)}=2H^+_{(aq)}+2e^-$	$E=-0,059pH$
3	$Sb(OH)_{3(0)}+H_2O_{(l)}=Sb(OH)_{2(0)}+H^+_{(aq)}$	$pH=2,17$
4	$Sb_{(s)}+2H_2O_{(l)}=Sb(OH)_{2(0)}+2H^+_{(aq)}+3e^-$	$E=0,002-0,039pH$
5	$Sb(OH)_{3(0)}+3H_2O_{(l)}=Sb(OH)_{6(0)}+3H^+_{(aq)}+2e^-$	$E=0,611-0,089pH$
6	$Sb_{(s)}+3H_2O_{(l)}=Sb(OH)_{3(0)}+3H^+_{(aq)}+3e^-$	$E=0,222-0,059pH$
7	$Sb(OH)_{2(0)}+4H_2O_{(l)}=Sb(OH)_{6(0)}+4H^+_{(aq)}+2e^-$	$E=0,729-0,118pH$
8	$SbH_{3(g)}=Sb_{(s)}+3H^+_{(aq)}+3e^-$	$E=-0,533-0,059pH$
9	$2Mn^{2+}_{(aq)}+2Sb(OH)_{2(0)}+3H_2O_{(l)}=Mn_2Sb_2O_7(s)+10H^+_{(aq)}+4e^-$	$E=0,4075-0,148$
10	$2Mn^{2+}_{(aq)}+2Sb(OH)_{3(0)}+H_2O_{(l)}=Mn_2Sb_2O_7(s)+8H^+_{(aq)}+4e^-$	$E=0,3813-0,118pH$
11	$2Sb_{(s)}+3H_2O_{(l)}+2HMnO_2^-(0)=Mn_2Sb_2O_7(s)+8H^+_{(aq)}+10e^-$	$E=-0,128-0,472pH$
12	$2Sb_{(s)}+2Mn^{2+}_{(aq)}+7H_2O_{(l)}=Mn_2Sb_2O_7(s)+14H^+_{(aq)}+10e^-$	$E=-0,2858-0,826pH$
13	$2Sb_{(s)}+3Mn^{2+}_{(aq)}+8H_2O_{(l)}=Mn_3(SbO_4)_2(s)+16H^+_{(aq)}+10e^-$	$E=0,325-0,0944pH$
14	$2Sb(OH)_{3(0)}+3Mn^{2+}_{(aq)}+2H_2O_{(l)}=Mn_3(SbO_4)_2(s)+10H^+_{(aq)}+4e^-$	$E=0,479-0,148pH$
15	$2Sb_{(s)}+3HMnO_2^-(0)+2H_2O_{(l)}=Mn_3(SbO_4)_2(s)+7H^+_{(aq)}+10e^-$	$E=-0,285-0,041pH$
16	$3Mn^{2+}_{(aq)}+2Sb(OH)_{2(0)}+4H_2O_{(l)}=Mn_3(SbO_4)_2(s)+12H^+_{(aq)}+4e^-$	$E=1,738-0,177pH$

Equations numbered from 9 to 16 in Table II correspond to the reactions of formation of various manganese antimonates (built based on Sb-H₂O and Mn-H₂O systems), in particular, the equations 9, 10, 11, 12 – borders of manganese antimonate stability of Mn₂Sb₂O₇ composition; equations 13, 14, 15, 16 - the stability limits of manganese antimonate of Mn₃(SbO₄)₂ composition.

An analysis of the E-pH diagram of Mn-Sb-H₂O system found that manganese antimonates compounds in oxidized, reducing aqueous media throughout the pH range at 25 °C and 1 atm are stable.

On Fig. 3, for the first time diagram of E-pH system of Mn-Bi-H₂O under standard conditions by combining private Bi-H₂O system diagram with of a private diagram of Mn-H₂O is shown. On E-pH diagram, line 1, 2 correspond to the upper and lower boundaries of water sustainability.

Reaction equations of Bi-H₂O system (numbered from 3 to 12 in Table III), indicated in the diagram by dotted lines correspond to all the possible interactions of the Bi-H₂O system, which shows the interaction and the existence region of bismuth ions: Bi⁰, Bi³⁺, BiOH²⁺, and bismuth oxides Bi₂O₃, Bi₄O₇, Bi₂O₄, Bi₂O₅, and also BiH₃.

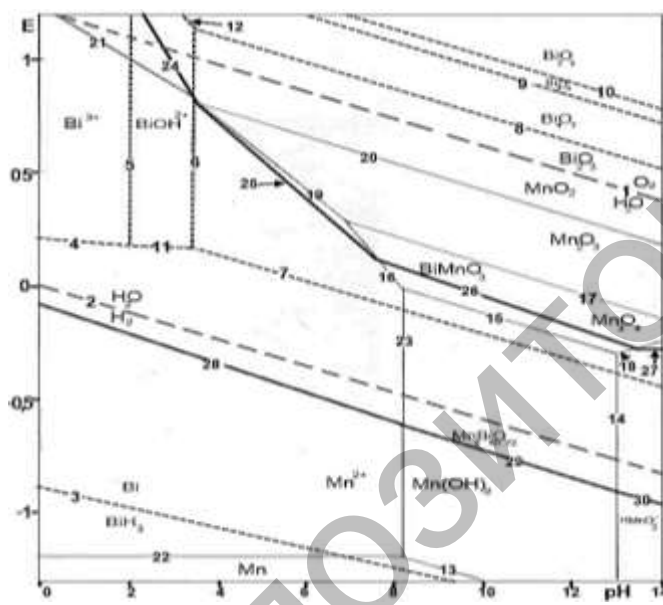


Fig.3 E-pH diagram of Mn-Bi-H₂O

The following reaction equations (from 13 to 23 in Table III) of Mn-H₂O system are indicated by thin solid lines, by which the interaction and the domain of existence of manganese ions are shown: Mn²⁺, HMnO₂⁻ oxides and manganese hydroxide Mn₂O₃, Mn₃O₄, MnO₂, Mn(OH)₂.

The equations numbered from 24 to 30 in Table III correspond to the region of existence of bismuth manganese compounds (built based on Bi-H₂O and Mn-H₂O systems), in particular the reactions under 28, 29, 30 numbers show the area of formation of manganese bismuthate composition Mn₈Bi₄₀O₇₂, and the lines 24, 25, 26, 27 - BiMnO₃ compound composition (stability area of the compounds is not limited in the considered anode region), the possibility of synthesizing

these compounds as solid phased, and also with hydrochemical methods is confirmed with known literature data [1], [2].

Compounds such as Bi₂Mn₄O₉, Bi₃Mn₅O₁₂ considering limiting interactions of the Bi-H₂O and Mn-H₂O systems were unable to reflect on this diagram.

TABLE III
SYSTEM INTERACTION EQUATIONS MN-BI-H₂O SYSTEM

№	Chemical reaction	Electrode reaction
1	H ₂ O(l)=O _{2(g)} +4H ⁺ (l)+4ē	E=1,23-0,059pH
2	H _{2(g)} =2H ⁺ (l)+2ē	E=-0,059pH
3	BiH _{3(g)} =Bi _(s) +3H ⁺ (l)+3ē	E=0,8197-0,0591pH
4	Bi _(s) =Bi ³⁺ (l)+3ē	E=0,22+0,02lg[Bi ³⁺]
5	Bi ³⁺ (l)+H ₂ O(l)=BiOH ²⁺ (l)+H ⁺ (l)	pH=2
6	2BiOH ²⁺ (l)+H ₂ O(l)=Bi ₂ O _{3(s)} +4H ⁺ (l)	lg[BiOH ²⁺]=6-2pH
7	2Bi _(s) +3H ₂ O(l)=Bi ₂ O _{3(s)} +6H ⁺ (l)+6ē	E=0,371-0,0591pH
8	2Bi ₂ O _{3(s)} +H ₂ O(l)=Bi ₄ O _{7(s)} +2H ⁺ (l)+2ē	E=1,338-0,0591pH
9	2Bi ₄ O _{7(s)} +H ₂ O(l)=2Bi ₂ O _{4(s)} +2H ⁺ (l)+2ē	E=1,541-0,0591pH
10	Bi ₂ O _{4(s)} +H ₂ O(l)=Bi ₂ O _{5(s)} +2H ⁺ (l)+2ē	E=1,607-0,0591pH
11	Bi _(s) +H ₂ O(l)=BiOH ²⁺ (l)+H ⁺ (l)+3ē	E=0,234-0,0197pH
12	4BiOH ²⁺ (l)+3H ₂ O(l)=Bi ₄ O _{7(s)} +10H ⁺ (l)+2ē	E=2,16-0,2295pH
13	Mn _(s) +2H ₂ O(l)=Mn(OH) _{2(s)} +2H ⁺ (l)+2ē	E=-0,727-0,059pH
14	Mn(OH) _{2(s)} +HMnO _{2(s)} +H ⁺ (l)=2ē	pH=12,9
15	3Mn(OH) _{2(s)} =Mn ₃ O _{4(s)} +2H ₂ O(l)+2H ⁺ (l)+2ē	E=0,402-0,059pH
16	3Mn ²⁺ (l)+4H ₂ O(l)=Mn ₃ O _{4(s)} +8H ⁺ (l)+2ē	E=1,912-0,236pH
17	2Mn ₂ O _{4(s)} +H ₂ O(l)=3Mn ₂ O _{3(s)} +2H ⁺ (l)+2ē	E=0,689-0,059pH
18	3HMnO _{2(l)} +H ⁺ (l)=Mn ₃ O _{4(s)} +2H ₂ O(l)+2ē	E=1,317+0,295pH
19	2Mn ²⁺ (l)+3H ₂ O(l)=Mn ₂ O _{3(s)} +6H ⁺ (l)+2ē	E=1,502-0,177pH
20	Mn ₂ O _{3(s)} +H ₂ O(l)=2MnO _{2(s)} +2H ⁺ (l)+2ē	E=1,014-0,059pH
21	Mn ²⁺ (l)+2H ₂ O(l)=MnO _{2(s)} +4H ⁺ (l)+2ē	E=1,258-0,118pH
22	Mn _(s) =Mn ²⁺ (l)+2ē	E=-1,209
23	Mn ²⁺ (l)+2H ₂ O(l)=Mn(OH) _{2(s)} +2H ⁺ (l)	lgK _{1}=-lg[Mn²⁺]-2pH}
24	Mn ²⁺ (l)+BiOH ²⁺ (l)+2H ₂ O(l)=BiMnO _{3(s)} +5H ⁺ (l)+ē	E=0,225-00,072pH
25	2Mn ²⁺ (l)+Bi ₂ O _{3(s)} +3H ₂ O(l)=2BiMnO _{3(s)} +6H ⁺ (l)+2ē	E=0,225-00,072pH
26	2Mn ₂ O _{4(s)} +3Bi ₂ O _{3(s)} +H ₂ O(l)=6BiMnO _{3(s)} +2H ⁺ (l)+2ē	E=0,225-00,072pH
27	2HMnO _{2(l)} +Bi ₂ O _{3(s)} =2BiMnO _{3(s)} +H ₂ O(l)+2ē	E=0,225-00,072pH
28	8Mn ²⁺ (l)+40Bi _(s) +72H ₂ O(l)=Mn ₈ Bi ₄₀ O _{72(s)} +144H ⁺ (l)+128ē	E=0,25-00,072pH
29	8Mn(OH) _{2(s)} +40Bi _(s) +56H ₂ O(l)=Mn ₈ Bi ₄₀ O _{72(s)} +128H ⁺ (l)+128ē	E=0,5-00,072pH
30	8HMnO _{2(l)} +40Bi _(s) +56H ₂ O(l)=Mn ₈ Bi ₄₀ O _{72(s)} +120H ⁺ (l)+128ē	E=0,225-00,072pH

An analysis of the E-pH diagram of Mn-Bi-H₂O system found that bismuthcontaining manganese compounds are stable throughout the whole pH range, wherein BiMnO₃ – in oxidized, Mn₈Bi₄₀O₇₂ - in oxidized and in recovering aqueous environment at 25°C and 1 atm.

III. CONCLUSION

Accordingly, based on thermodynamic analysis using E-pH diagrams can it may be stated that arsenates, antimonates, and manganese bismuthate are stable compounds in acid environment at 25° C and 1 atm. The practical value of these studies will be tested in laboratory experiments to clean copper electrolyte from arsenic, antimony and bismuth manganese-containing precipitators.

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