UDC 536.7

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Comparative analysis of arsenates, antimonates and calcium bismuthates based on *E*–pH diagrams

The article presents the potential-pH diagram systems Ca–As–H_2O, Ca–Sb–H_2O, Ca–Bi–H_2O and the analysis of these systems. The stability region is shown for the followings: $Ca_3(AsO_4)_2$, $Ca_3(AsO_4)_2 \cdot 4H_2O$, $Ca(AsO_2)_2$, $Ca(SbO_3)_2$, $Ca_2Sb_2O_7$, $Ca_3(SbO_4)_2$, $Ca_5Bi_{14}O_{26}$, $Ca_2Bi_2O_5$, $CaBi_2O_4$ in oxidizing, recovering and aquatic environments. The data obtained can be used in predicting the occurrence of hydrometallurgical processes, due to the fact that the E–pH diagram characterizes the behavior of ions in solutions of the compounds.

Key words: diagram of the potential–pH, calcium arsenate, calcium antimonate, calcium bismuthate, thermodynamic analysis.

During the production of non-ferrous metals, arsenic, antimony and bismuth are considered as bad contaminants. During copper electrolysis their transition from anode copper in solution happens as a result contamination of the electrolyte occurs. The accumulation of significant amounts of harmful impurities in the electrolyte can lead to increased resistance, viscosity of the solution, as well as the overuse of electricity, and therefore, there is a problem of cleaning electrolyte copper production. The world practice for these purposes uses different methods, whereas the analysis shows that there is still a question of purifying electrolyte, as applied methods do not allow to reach deep purity solutions.

The aim of this study is a comparative analysis of arsenates, antimonates and calcium bismuthates in order to predict the behavior of arsenic, antimony and bismuth in the process of hydrolytic precipitation of calcium compounds.

In metallurgy, the main characteristics of hydro and pyrometallurgical processes are thermodynamic quantities of reaction components that enable to predict the direction of the process, the probability of the meeting, under certain conditions, the value of the thermal effect.

Characteristic physicochemical properties of aqueous solutions, which define the process of dissolution and precipitation of various compounds are pH and electrochemical or redox potential (*E*).

Thermodynamic analysis, based on the construction of diagrams of *E*–pH is a chemical and thermodynamic basis for addressing assessment of the stability limits of the compounds involved in hydrometallurgical processes to flow any reaction and directed synthesis that allows you to monitor the progress of the processes and effectively carry out these processes in industrial environments [1, 2].

Arsenic-, antimony- and bismuth containing systems are insufficiently studied, despite the fact that the elements are circulating in many non-ferrous metallurgical processes, complicating the process flow, thereby reducing their cost-effectiveness. In this regard, based on charting *E*–pH systems of Ca–As–H_2O, Ca–Sb–H_2O, Ca–Bi–H_2O, we graphically show the stability boundaries and formation of calcium arsenates composition of $Ca_3(AsO_4)_2$, $Ca_3(AsO_4)_2 \cdot 4H_2O$, $Ca(AsO_2)_2$–H_2O, calcium antimonates — $Ca(SbO_3)_2$, $Ca_2Sb_2O_7$, $Ca_3(SbO_4)_2$ and calcium bismuthates — $Ca_5Bi_{14}O_{26}$, $Ca_2Bi_2O_5$, $CaBi_2O_4$.

Calculated (Table 1) and constructed (Fig. 1) diagram *E*–pH of the system Ca–As–H_2O at standard conditions (25 ºC and 1 atm. Total pressure) by combining the private system diagram As–H_2O with private diagram of Ca–H_2O is shown.

According to the *E*–pH diagram of the Ca–As–H_2O system forming calcium arsenates in strongly acidic solutions is preferably than arsenite formation of calcium because for deposition of arsenic as calcium arsenite composition $Ca(AsO_2)_2$ solution pH should not be lower than 4.26.

Calculated (Table 2) and constructed (Fig. 2) diagram *E*–pH of the Ca–Sb–H_2O at standard conditions (25 °C and 1 atm. Total pressure) by combining the private system diagram of Sb–H_2O with private diagram of Ca–H_2O is shown.

Table 1

Calculation equations of interacting systems $Ca(AsO_2)_2 – Ca_3(AsO_4)_2 – H_2O$ at 25 ºC

№	Chemical reaction	Electrode reaction
1	$H_2O_{(L)}{=}O_{2(g)}+4H^+_{(L)}+4\bar{e}$	E = 1,23–0,059pH
2	$H_{2(g)}{=}2H^+_{(L)}+2\bar{e}$	E = –0,059pH
3	$H_3AsO_{3(L)}+H_2O_{(L)}{=}H_3AsO_{4(L)}+2H^+_{(L)}+2\bar{e}$	E = 0,586+0,029 lg[H_3AsO_4]–0,029 lg[H_3AsO_3]–0,059pH
4	$H_3AsO_{4(L)}{=}H_2AsO^-_{4\,(L)}+H^+_{(L)}$	lgК$_p$ = lg[$H_2AsO_4^-$]–lg[H_3AsO_4]–pH; pH=2,19
5	$H_2AsO^-_{3\,(L)}{=}HAsO_3^{2-}{}_{(L)}+H^+_{(L)}$	lgК$_p$ = lg[$HAsO_3^{2-}$]–lg[H_2AsO_3]–pH; pH=12,10
6	$HAsO_3^{2-}{}_{(L)}{=}H^+_{(L)}+AsO_3^{3-}{}_{(L)}$	lgК$_p$ = lg[AsO_3^{3-}]–lg[$HAsO_3^{2-}$]–pH; pH=13,41
7	$H_2AsO_{3(L)}^-+H_2O_{(L)}{=}AsO_4^{3-}{}_{(L)}+4H^+_{(L)}+2\bar{e}$	E = 0,925–0,029 lg[$H_2AsO_3^-$]+0,029 lg[AsO_4^{3-}]–0,118pH
8	$HAsO_3^{2-}{}_{(L)}+H_2O_{(L)}{=}AsO_4^{3-}{}_{(L)}+3H^+_{(L)}+2\bar{e}$	E = 0,567–0,029 lg[$HAsO_3^{2-}$]+0,029 lg[AsO_4^{3-}]–0,088pH
9	$As_{(т)}+3H_2O_{(L)}{=}HAsO_3^{2-}{}_{(L)}+5H^+_{(L)}+3\bar{e}$	E = 0,647+0,019 lg[$HAsO_3^{2-}$]–0,098pH
10	$AsO_3^{3-}{}_{(L)}+H_2O_{(L)}{=}AsO_4^{3-}{}_{(L)}+2H^+_{(L)}+2\bar{e}$	E = 0,170+0,029 lg[AsO_4^{3-}]–0,029 lg[AsO_3^{3-}]–0,059pH
11	$As_{(т)}+3H_2O_{(L)}{=}AsO_3^{3-}{}_{(L)}+6H^+_{(L)}+3\bar{e}$	E = 0,912+0,0196 lg[AsO_3^{3-}]–0,118pH
12	$HAsO_4^{2-}{}_{(L)}{=}H^+_{(L)}+AsO_4^{3-}{}_{(L)}$	lgК$_p$ = lg[AsO_4^{3-}]–lg[$HAsO_4^{2-}$]–pH; pH=11,51
13	$H_2AsO^-_{4\,(L)}{=}HAsO_4^{2-}{}_{(L)}+H^+_{(L)}$	lgК$_p$ = lg[$HAsO_4^{2-}$]–lg[$H_2AsO_4^-$]–pH; pH=6,79
14	$H_2AsO^-_{3\,(L)}+H_2O_{(L)}{=}HAsO_4^{2-}{}_{(L)}+3H^+_{(L)}+2\bar{e}$	E = 0,585+0,029 lg[$HAsO_4^{2-}$]–0,029 lg[$H_2AsO_3^-$]–0,088pH
15	$As_{(т)}+3H_2O_{(L)}{=}H_2AsO^-_{3\,(L)}+4H^+_{(L)}+3\bar{e}$	E = 0,4085+0,0196 lg[$H_2AsO_3^-$]–0,078pH
16	$As_{(т)}+3H_2O_{(L)}{=}H_3AsO_{3(L)}+3H^+_{(L)}+3\bar{e}$	E = 0,226+0,0196 lg[H_3AsO_3]–0,059pH
17	$AsH_{3(g)}{=}As_{(т)}+3H^++3\bar{e}$	E = –0,6268–0,059pH
18	$H_3AsO_{3(L)}+H_2O_{(L)}{=}HAsO_4^{2-}{}_{(L)}+4H^+_{(L)}+2\bar{e}$	E = 0,858+0,029 lg[$HAsO_4^{2-}$]–0,029 lg[H_3AsO_3]–0,118pH
19	$H_3AsO_{3(L)}{=}H_2AsO^-_{3\,(L)}+H^+_{(L)}$	lgК$_p$ = lg[$H_2AsO_3^-$]–lg[H_3AsO_3]–pH; pH=9,24
20	$H_3AsO_{4(L)}{=}H_2AsO^-_{4\,(L)}+H^+_{(L)}$	lgК$_p$ = lg[$H_2AsO_4^-$]–lg[H_3AsO_4]–pH; pH=2,19
21	$3Ca^{2+}+2H_3AsO_4{=}Ca_3(AsO_4)_2+6H^+$	lgК$_p$ = –3lg[Ca^{2+}]–2 lg[H_3AsO_4]–6pH, pH=2,37
22	$3Ca(AsO_2)_2+8H_2O{=}Ca_3(AsO_4)_2+4H_3AsO_3+4H^++4\bar{e}$	E = 0.3354–0.059pH
23	$Ca^{2+}+2H_3AsO_3{=}Ca(AsO_2)_2+2H_2O+2H^+$	lgК$_p$ = –lg[Ca^{2+}]–2 lg[H_3AsO_3]–2pH pH=4,26
24	$3Ca^{2+}+2H_3AsO_3+2H_2O{=}Ca_3(AsO_4)_2+10H^++4\bar{e}$	E = 0.97975–0.1475pH
25	$Ca^{2+}+2As+4H_2O\ {=}Ca(AsO_2)_2+8H^++6\ \bar{e}$	E = 0,34983–0.07867pH
26	$Ca_3(AsO_4)_2+Ca^{2+}+6H_2O =$ $= Ca_3(AsO_4)_2\cdot 4\ H_2O + +Ca(OH)_2\ +2H^+$	lgК$_p$ = –lg[Ca^{2+}]–2pH; pH=11,20
27	$Ca_3(AsO_4)_2\cdot 4H_2O+2\ H_2O{=}3Ca(OH)_2+2AsO_4^{3-}+6H^+$	lgК$_p$ = 2 lg[AsO_4^{3-}]–6pH; pH=14,20

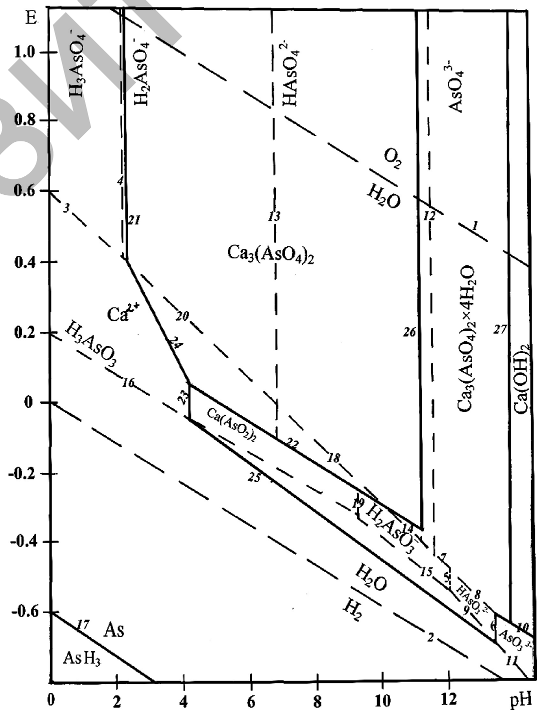

Figure 1. Diagram of E-pH system $Ca(AsO_2)_2$ — $Ca_3(AsO_4)_2$ — H_2O

Table 2

Calculation equations of interacting systems Ca–Sb–H_2O at 25 ºC

№	Reaction equation	Electrode reaction
1	$H_2O_{(L)}=O_{2(g)}+4H^+_{(L)}+4\bar{e}$	$E = 1{,}23–0{,}059pH$
2	$H_{2(g)}=2H^+_{(L)}+2\bar{e}$	$E = –0{,}059pH$
3	$Sb(OH)_2^+ + H_2O= Sb(OH)_3+H^+$	pH=2,17
4	$Sb + 2H_2O= Sb(OH)_2^++2H^++3\bar{e}$	$E = 0{,}199 + 0{,}0197 \lg[Sb(OH)_2^+]–0{,}039pH$
5	$Sb(OH)_3+ 3H_2O= Sb(OH)_6^{—} +3H^++2\bar{e}$	$E = 0{,}729 + 0{,}118 \lg[Sb(OH)_6^-]–0{,}089pH$
6	$Sb + 3H_2O= Sb(OH)_3+3H^++3\bar{e}$	$E = 0{,}222–0{,}059pH$
7	$Sb(OH)_2^+ +4 H_2O= Sb(OH)_6^{—} +4H^++2\bar{e}$	E = 0,729 +0,0295 lg$[Sb(OH)_6^-]$–0,0295 lg$[Sb(OH)_2^+]$– –0,118pH
8	$SbH_3= Sb+3H^++3\bar{e}$	E = –0,51–0,0198 lgPSb_3–0,059 pH
9	$3Ca^{2+}+2Sb(OH)_2^++4H_2O=Ca_3(SbO_4)_2+12H^++4\bar{e}$	$E = 0{,}42–0{,}0443 \lg[Ca^{2+}]–0{,}0295 \lg[Sb(OH)_2^+]–0{,}177pH$
10	$3Ca^{2+}+2Sb(OH)_3+2H_2O=Ca_3(SbO_4)_2+10H^++4\bar{e}$	$E = 0{,}386–0{,}0443 \lg[Ca^{2+}]–0{,}148pH$
11	$3Ca^{2+}+2Sb+8H_2O=Ca_3(SbO_4)_2+16H^++10\bar{e}$	$E = 0{,}386–0{,}018 \lg[Ca^{2+}]–0{,}094pH$
12	$2Ca^{2+}+2Sb(OH)_2^++4H_2O=Ca_3(SbO_4)_2+12H^++4\bar{e}$	$E = 0{,}42–0{,}0443 \lg[Ca^{2+}]–0{,}0295 \lg[Sb(OH)_2^+]–0{,}177pH$
13	$2Ca^{2+}+2Sb(OH)_3+H_2O= Ca_2Sb_2O_7+8H^++4\bar{e}$	$E = 0{,}316–0{,}0295 \lg[Ca^{2+}]–0{,}118pH$
14	$2Ca^{2+}+2Sb+7H_2O= Ca_2Sb_2O_7+14H^++10\bar{e}$	$E = 0{,}386–0{,}018 \lg[Ca^{2+}]–0{,}094pH$
15	$Ca^{2+}+2Sb(OH)_3=Ca(SbO_3)_2+6H^++4\bar{e}$	$E = –0{,}95–0{,}0148 \lg[Ca^{2+}]–0{,}089pH$
16	$Ca^{2+}+2Sb+6H_2O= Ca(SbO_3)_2+12H^++10\bar{e}$	$E = 0{,}23–0{,}006 \lg[Ca^{2+}]–0{,}071pH$
17	$2Sb+ 3Ca(OH)_2+2H_2O=Ca_3(SbO_4)_2+10H^++10\bar{e}$	$E = –0{,}120–0{,}059pH$
18	$2Sb+ 2Ca(OH)_2+3H_2O=Ca_2Sb_2O_7+10H^++10\bar{e}$	$E = –0{,}012–0{,}059pH$
19	$2Sb+Ca(OH)_2+4H_2O=Ca(SbO_3)_2+10H^++10\bar{e}$	$E = –0{,}0944–0{,}059pH$

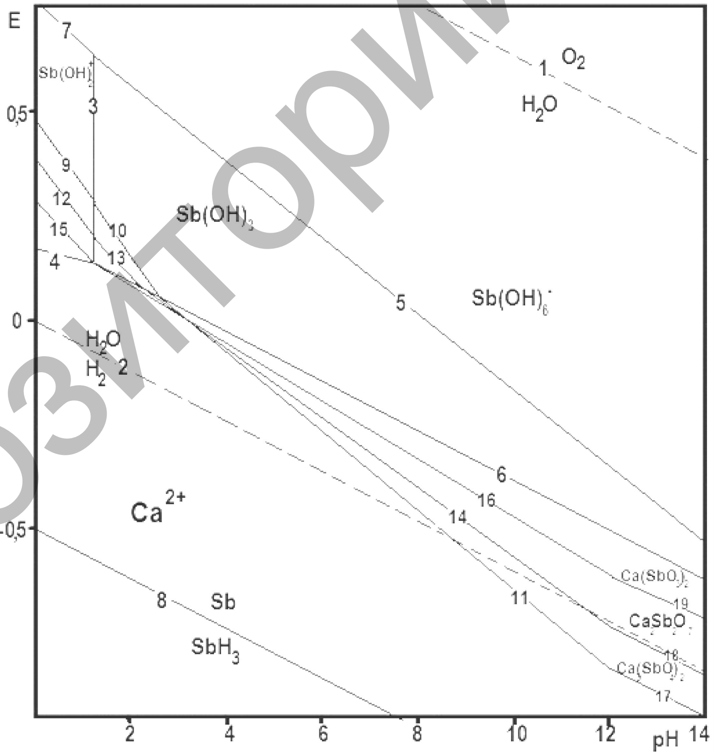

Figure 2. Diagram of *E*–pH system Ca–Sb–H_2O

The first two equations are the equations of the reaction the upper and lower boundaries of the sustainability of water (reaction equations 1, 2). The following reactions at number 3 to 8 meet all the possible interactions of Sb–H_2O, which shows the interaction and existence of dissolved Antimony: $Sb(OH)_2^+$, $Sb(OH)_3$, $Sb(OH)_6^-$, SbH_3 and Sb^0.

Equations numbered from 9 to 19 correspond to the reactions of formation of various calcium antimonates (built based on Sb–H_2O and Ca–H_2O systems). In particular the equations 9, 10, 11, 17 — the boundaries of sustainability of calcium antimonate structure $Ca_3(SbO_4)_2$; Equation 12, 13, 14, 18 — the stability boundary structure of calcium antimonate$Ca_2Sb_2O_7$; Equation 15, 16, 19 — the stability boundary structure of calcium antimonate $Ca(SbO_3)_2$.

Calculated (Table 3) and built (Fig. 3) Diagram *E*–pH of the system Ca–Bi–H_2O at standard conditions (25 °C and 1 atm. Total pressure) by combining the private system diagram of Bi-H_2O with private diagram of Ca–H_2O is shown [3, 4].

Table 3

Calculation equations of interacting systems Ca–Bi–H_2O at 25 ºC

№	Reaction equation	Electrode reaction
1	$H_2O_{(L)}=O_{2(g)}+4H^+_{(L)}+4\bar{e}$	$E = 1{,}23–0{,}059pH$
2	$H_{2(g)}=2H^+_{(L)}+2\bar{e}$	$E = –0{,}059pH$
3	$BiH_3 =Bi+3H^++3\bar{e}$	$E = 0{,}8–0{,}0591pH–0{,}0197lgP_{BiH3}$
4	$Bi=Bi^{3+}+3\bar{e}$	$E = 0{,}215+0{,}0197lg[Bi^{3+}]$
5	$Bi^{3+}+H_2O=BiOH^{2+}+H^+$	$lg[BiOH^{2+}]/ lg[Bi^{3+}] = –2{,}0+pH$
6	$2BiOH^{2+}+H_2O=Bi_2O_3+4H^+$	$lg[BiOH^{2+}] = 5{,}96–2pH$
7	$2Bi+3H_2O= Bi_2O_3+6H^+ +6\bar{e}$	$E = 0{,}371–0{,}0591pH$
8	$Bi+H_2O= BiOH^{2+}+H^++3\bar{e}$	$E = 0{,}254–0{,}0197pH+0{,}0197lg[BiOH^{2+}]$
9	$2Bi^{3+}+5H_2O=Bi_2O_5+10H^++4\bar{e}$	$E = 1{,}759–0{,}1477pH–0{,}0295lg[Bi^{3+}]$
10	$2BiOH^{2+}+2H_2O=Bi_2O_4+6H^++2\bar{e}$	$E = 1{,}792–0{,}1773pH–0{,}0591lg[BiOH^{2+}]$
11	$4BiOH^{2+}+3H_2O=Bi_4O_7+10H^++2\bar{e}$	$E = 2{,}042–0{,}2295pH–0{,}1182lg[BiOH^{2+}]$
12	$2Bi_2O_3+H_2O=Bi_4O_7+2H^++2\bar{e}$	$E = 1{,}338–0{,}0591pH$
13	$2Bi_4O_7+H_2O=2Bi_2O_4+2H^++2\bar{e}$	$E = 1{,}541–0{,}0591pH$
14	$Bi_2O_4+H_2O=Bi_2O_5+2H^++2\bar{e}$	$E = 1{,}607–0{,}0591pH$
15	$2Ca^{2+} +6Bi^{3+}+11H_2O=Ca_2Bi_6O_{11}+22H^+$	$pH = 0{,}42$
16	$2Ca^{2+} +6Bi^0+11H_2O=Ca_2Bi_6O_{11}+22H^++18\bar{e}$	$E = 0{,}225–00{,}072pH$
17	$CaBi_2O_4+Ca^{2+}+4Bi^{3+}+7H_2O=Ca_2Bi_6O_{11}+14H^+$	$pH = 1{,}0$
18	$Ca_2Bi_2O_5 +4Bi^{3+}+6H_2O=Ca_2Bi_6O_{11}+12H^+$	$pH = 1{,}5$
19	$Ca_5Bi_{14}O_{26} +2BiOH^{2+}+H_2O=5Ca_2Bi_6O_{11}+4H^+$	$pH = 3{,}73$

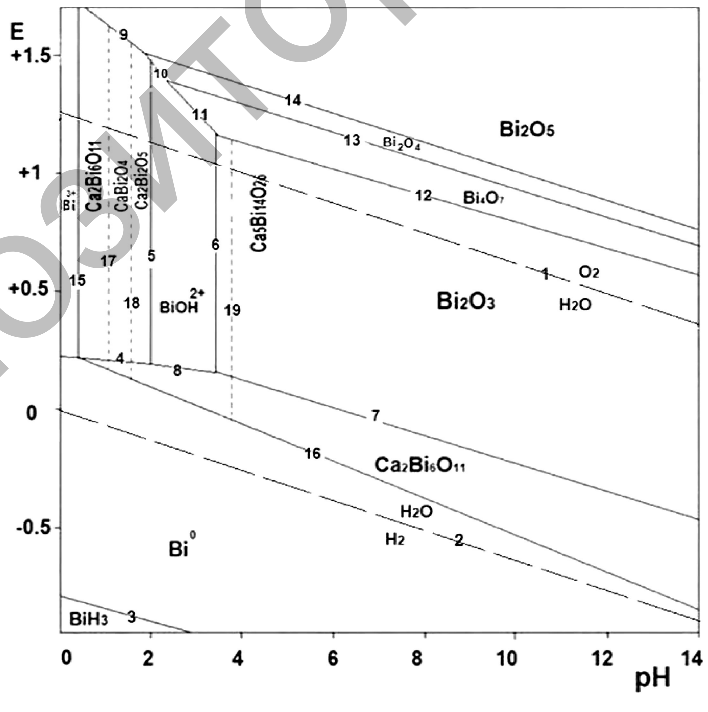

Figure 3. Diagram of *E*–pH systems Ca–Bi–H_2O

The first two equations are the equations of the reaction the upper and lower boundaries of the sustainability of water (reaction equations 1, 2). The following reactions at number from 3 to 14 meet all the possible interactions of the system Bi–H_2O, which shows the interactions and existence of bismuth ions: Bi^0, Bi^{3+}, $BiOH^{2+}$, BiH_3 and bismuth oxide Bi_2O_3, Bi_4O_7, Bi_2O_4, Bi_2O_5.

Equations under the number of 15 to 19 corresponds to the region of existence of calcium bismuthates (systems are built based on Bi–H_2O and Ca–H_2O), in particular, the equations 15 and 16 — the existence of the border calcium bismuthate composition $Ca_2Bi_6O_{11}$. Dash-dotted lines correspond to the boundaries of possible transition bismuthate calcium $Ca_2Bi_6O_{11}$ the next bismuthates: $CaBi_2O_4$ (reaction equation 17), $Ca_2Bi_2O_5$ (reaction equation 18), $Ca_5Bi_{14}O_{26}$ (reaction equation 19).

Such bismuthates as $Ca_3Bi_4O_9$, Ca_7Bi_6O16, $Sa_7Bi_{10}O_{22}$, which subject to limiting interactions of Bi–H_2O system and Ca–H_2O, on this chart are not reflected.

Based on the analysis of the set of diagrams results show that arsenates, antimonates and calcium bismuthates are stable compounds in oxidized, recovered and aqueous media. Calcium arsenate are stable in an oxidizing environment at $E > 0{,}4$ V and the pH range of 2–14; calcium antimonates and calcium bismuthates — throughout the whole pH range. Increase in the number of metal properties in As–Sb–Bi leads to increase of the stability region in the row arsenate – antimonate – calcium bismuthate in acid areas.

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Кальцийдің арсенаттарын, антимонаттарын және висмутаттарын *E*–pH диаграммасы негізінде салыстыра отырып талдау

Мақалада Ca–As–H_2O, Ca–Sb–H_2O, Ca–Bi–H_2O жүйелерінің *E*–pH диаграммасы көрсетілген және оған талдау жүргізілген. $Ca_3(AsO_4)_2$, $Ca_3(AsO_4)_2{\cdot}4H_2O$, $Ca(AsO_2)_2$, $Ca(SbO_3)_2$, $Ca_2Sb_2O_7$, $Ca_3(SbO_4)_2$, $Ca_5Bi_{14}O_{26}$, $Ca_2Bi_2O_5$, $CaBi_2O_4$ сияқты тұрақты қосылыстардың тұрақтылық аймағы белгіленген. Мақаладағы мәліметтер гидрометаллургия саласында өте қызықты болып табылады, себебі *E*–pH диаграммасы иондар мен қосылыстардың ерітіндідегі қасиетін сипаттайды.

Х.Б.Омаров, З.Б.Абсат, С.К.Алдабергенова, Н.Ж.Рахимжанова, А.Б.Сиязова

Сравнительный анализ арсенатов, антимонатов и висмутатов кальция на основе диаграммы *E*–pH

В статье представлены диаграммы потенциал–pH систем Ca–As–H_2O, Ca–Sb–H_2O, Ca–Bi–H_2O и проведен анализ данных систем. Показаны области устойчивости $Ca_3(AsO_4)_2$, $Ca_3(AsO_4)_2{\cdot}4H_2O$, $Ca(AsO_2)_2$, $Ca(SbO_3)_2$, $Ca_2Sb_2O_7$, $Ca_3(SbO_4)_2$, $Ca_5Bi_{14}O_{26}$, $Ca_2Bi_2O_5$, $CaBi_2O_4$, которые являются устойчивыми соединениями. Данные статьи представляют интерес в гидрометаллургических процессах, в связи с тем, что диаграмма E-pH характеризует поведение ионов, соединений в растворах.

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