

MODELLING THE CONDITIONS OF CIRCULATING WATER SUPPLY FOR A COPPER ORE PROCESSING PLANT

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ABSTRACT

There is carried out a quantitative assessment of the changes in the circulating water composition under the influence of its conditioning method in a circulating water supply system of the Balkhash Concentrator Plant. Research objects are circulating water model mixtures which are reuse in copper ores flotation after clarification in a tailings dam. They are obtained in a laboratory because of modelling the mixing and storage conditions of enrichment tailings from the Balkhash Concentrator Plant and acid effluents neutralization sludge from the Balkhash Copper Smelter Plant with industrial effluents from other enterprises in Balkhash region. There is considers two schemes for conditioning of recycle water in the process water supply system: by mixing clarified water obtained during the combined or separate waste storage (enrichment tailings and acid effluents neutralization sludge). Studies have shown that after mixing these flows in the tail collector and their combined storage in the tailings dam chemical and physico-chemical processes occur that contribute to the removal of several pollutants (copper, arsenic, iron, zinc, cadmium, and nickel) from circulating water, which can be explained by the binding of cations these elements into insoluble compounds. Based on the results obtained, it is recommended to use a combined waste storage technology for the circulating water conditioning.

Keywords: mineral processing, technological waters, industrial effluents, neutralization sludge, wastewater treatment, tailings dam, combined waste storage.

INTRODUCTION

The currently applied technologies for mining, enrichment and processing of ores require improvement, and first, the introduction of closed circuits with the most complete water circulation, associated extraction of valuable components and minimization of environmental pollution. An important task to be solved in the organization of circulating water supply systems at mining and processing enterprises is the

maximum use in the production of complex chemical composition effluents, which are formed as a result of related processes at leaching or hydrometallurgy plants, or at other industrial complexes, such as a site acid effluents neutralization (AES) [1, 2].

At ore processing plants, the main flow of process water is formed by clarified water entering through the water intake well from the tailings dam [1, 3]. Insoluble fine suspended solids, various ions and organic chemicals dissolved in recycled water affect

its properties determining its use in flotation processes [4]. Increasing use of recycle water in flotation without removal these impurities has often negative effects on recovery and selectivity since several of cationic and anionic impurities function as activators or depressants, some organic compounds are surface active or function as dispersants or flocculants [5]. The main harmful impurities in wastewater are various organic and inorganic flotation reagents, heavy metal ions, sulfates, sulfoxide ions, etc. [4, 6, 7]. Therefore, wastewater reuse and the development of measures to reduce or completely stop their discharge is the main trend in the world enrichment practice to achieve clean production.

In recent years, a wide range of treatment technologies such as chemical precipitation, adsorption, membrane filtration, electro dialysis, and photocatalysis, etc. have been developed for heavy metal removal from contaminated wastewater [8]. Among them chemical precipitation and adsorption methods are more often used [4]. Although, the physical separation by sedimentation in tailings pond has never been viewed as sufficient step for guarantying the desired purification degree for the flotation wastewater, the most of concentrators operating do treat their flotation effluents by classical schemes utilizing settling ponds for clarification [9].

It was found in Milovanov's research that with the endless return of wastewater into circulation, the content of substances accumulated in the circulating water changes insignificantly [3, 10]. That fact made it possible to organize closed circulating water supply systems. As a result of some technical solutions developed by the research and design institutes such as State Scientific Production Association of Industrial Ecology "Kazmekhanobr", "Unipromed" Institute, "Uralmekhanobr" JSC, State Research Institute of Non-Ferrous Metals "Gintsvetmet" JSC, "Mekhanobr Engineering" JSC, some major ore processing plants in Kazakhstan and Russia have implemented a full water circulation into their technology [7]. At many mining and processing enterprises, circulating water entering the tailings dam is formed due to the liquid phase of enrichment tailings and mine waters having a pH value of 11.5 - 12.5, high contents of sulfoxide ions and complex compounds. At mining and metallurgical enterprises, which include both a mining and processing production and a chemical and metallurgical one, circulating water is often formed by mixing in the tailings

dam wastewater from several shops: processing, copper smelting, chemical (sulphuric acid, superphosphate), as well as mine waters of the mining shop. Values pH and hardness of such recycled waters are lower, they have low content of sulfoxides also [10].

The qualitative ion-molecular composition of pulp liquid phase and wastewater when using fresh and recycled water is almost the same. However, the quantitative ionic-molecular composition of the liquid phase changes significantly in the case of recycled water, which has a noticeable effect on flotation results: on liquid-phase reactions involving the used flotation reagents (xanthate, dithiophosphate), on the composition, formation, and fixation of surface compounds on minerals.

The heterogeneous chemical nature of industrial effluents and the different contribution each of them to a tailings dam debit, as well as the period to get equilibrium that cannot be determined by theoretical methods, create the need for modelling this process in the laboratory.

In this research, there is carried out a quantitative assessment of the change in the recycled water composition under the influence of methods its preparation and storage in the circulating water supply system at the Balkhash Concentrator Plant which is part of the Balkhash production site "Kazakhmys Holding" LLP.

This study considers two schemes for conditioning circulating water: by mixing clarified water obtained with combined or separate storage of Balkhash Concentrator Plant (BCP) waste (enrichment tailings) and Balkhash Copper Smelter Plant (BCSP) waste (acid effluents neutralization sludge) in the tailings dam, with industrial effluents from other enterprises on the Balkhash site "Kazakhmys Holding" LLP [11 - 14].

Effluents from mining and processing enterprises and related technological processes are classified as large-scale industrial waste products. They are multicomponent and compositionally heterogeneous systems. Their most complete use is achieved by organizing circulating water supply systems in which almost all effluents are recycled. Most often, these schemes provide for the direction of circulating water directly to the enrichment process [15].

Process water used in flotation is an active component of the pulp liquid phase, which ensures the interaction of flotation reagents with the mineral surface

and must comply with certain chemical and physical parameters [6, 10].

From the point of view of saving flotation reagents, it is of interest to keep some of them in wastewater. Accounting for the presence of residual amounts of flotation reagents when using recycled water is a potential tool to reduce flotation costs. One of these components is the sulfide ion, the presence of which in circulating water will save sodium sulfide.

From the point of view of improving circulating water technological properties, the simplest and most effective way is the chemical binding of heavy metal ions into insoluble compounds using precipitant ions (carbonate, silicate, hydroxyl) [1].

To select the best conditions for deposition, it is necessary to establish their mechanisms. However, it is well known that ion exchange reactions in aqueous solutions, in most cases, proceed at a high rate, which makes it impossible to evaluate process kinetics by generally available methods. On the one hand, the complexity of measuring these reaction rates hinders the formulation of theoretical conclusions. But, on the other hand, the chemical composition of resulting solutions during subsequent their storage will no longer undergo changes associated with ion exchange reactions, which allows us to draw empirical conclusions.

For large-capacity industries, an alternative to reagent treatment methods is the option of conditioning circulating water by preliminary mixing of alkaline and acidic wastewater (to regulate pH) or wastewater containing significant concentrations of heavy metal ions and precipitant ions [15, 16]. At the Balkhash Mining and Metallurgical Combine, effluents from BCP, shops of BCSP, hydraulic ash sluicing system of Balkhash Combined Heat and Power Plant (BCHPP), and other enterprises located in the immediate vicinity, as well as industrial storm sewer effluents and drainage water are considered as such sources for conditioning.

EXPERIMENTAL

Materials

The research objects in this study are model mixtures of circulating water returned to the BCP after clarification into the tailings dam, obtained in laboratory because of modelling the mixing and storage conditions of the following samples:

- enrichment tailings of BCP from the gravity tail collector,

- acid effluents neutralization sludge of BCSP at the entrance to the tail collector BCP, which are formed because of neutralization acid effluents and sulfuric acid with limestone (ST RK 2650 - 2015) at the neutralization site in the sulfuric acid shop of BCSP,

- composite wastes obtained because of preliminary mixing enrichment tailings BCP and acid effluents neutralization sludge BCSP under production conditions in different proportions,

- industrial effluents from enterprises in the Balkhash region, among which included effluents from a machinery and repair plant, a non-ferrous metal processing plant, as well as a copper electrolysis shop, a charge preparation shop, and an oxygen production plant of BCSP,

- clarified water from the hydraulic ash sluicing system (HASS) of BCHPP,

- effluents from industrial storm sewers (ISS) at BCP and BCSP production facilities.

Preparation of composite samples

The preparation of composite samples was carried out in accordance with two waste storage schemes: combined waste storage (Scheme A) and separate waste storage (Scheme B). In each scheme, two options for the operation of the acid effluents neutralization site were considered. Increasing productivity of the neutralization site of BCSP due to effluents from the sulfuric acid shop considered in the option 2.

Samples enrichment tailings of BCP, acid effluents neutralization sludge of BCSP, and industrial effluents from abovementioned enterprises were taken at the production sites. A composite sample was prepared in a 5 dm³ container by successively adding all the components. According to Scheme A, enrichment tailings of BCP were mixed with acid effluents neutralization sludge of BCSP and industrial effluents from other enterprises in proportions determined from their hourly flow rate to the tailings dam. According to Scheme B, enrichment tailings of BCP were mixed only with industrial effluents from other enterprises in determined proportions and stored separately from acid effluents neutralization sludge.

To prepare composite samples according to Scheme B (separate waste storage), enrichment tailings

and industrial effluents from other enterprises were sequentially added to a 5 dm³ container in the proportions indicated in Table 1.

To prepare composite samples according to Scheme A (combined waste storage), enrichment tailings, industrial effluents from other enterprises and acidic effluents neutralization sludge were sequentially added to a 5 dm³ container in the proportions indicated in Table 1. In Scheme A2, proportions for mixing were determined considering the increase in productivity the AEN section (due to the increase in the productivity of the sulfuric acid shop).

As a result, 9 composite samples of pulp entering the tailings dam were obtained:

- samples 1_T - 3_T (according to schemes B1 and B2) during separate storage enrichment tailings (T) mixed with industrial effluents,

- samples 1_{ST} - 3_{ST} (according to Scheme A1) and 4_{ST} - 6_{ST} (according to scheme A2) during combine storage of enrichment tailings (T) mixed with industrial effluents and acid effluents neutralization sludge (S).

Samples 1_S - 3_S of neutralization sludge (S) were taken at the acid effluents neutralization site of BCSP also.

Preparation of circulating water model mixtures

Clarified water of the composite samples pulp (prepared according to schemes A and B) was mixed with clarified water from the hydraulic ash sluicing system of BCHPP, with effluents from industrial storm sewers at BCP and BCSP production facilities in proportions which were determined according to their hourly flow rate. The simulation also considered the return of drainage water to the tailings dam.

For each waste storage scheme (A1, A2, B1, and B2), three circulating water model mixtures were prepared to calculate the average statistical values of parameters analysed in this research.

Modeling of circulating water according to scheme A

In the tailing dam, clarified water from the pulp of composite samples obtained according to schemes A is mixed with clarified water from the section of hydraulic ash sluicing system (HASS) of BCHPP, with industrial storm sewage (ISS) effluents from BCP and BCSP facilities in the proportions indicated in Table 2. The modelling also considers the return of drainage water (DW) to the tailings dam.

Table 1. Proportions for composite samples formation.

Industrial wastewater name	Scheme A1 samples 1 _{ST} - 3 _{ST}			Scheme A2 samples 4 _{ST} - 6 _{ST}			Schemes B1 and B2 samples 1 _T - 3 _T		
	Flow rate, m ³ h ⁻¹	Mixing proportions, decimal quantity	Volume in composite sample, dm ³	Flow rate, m ³ h ⁻¹	Mixing proportions, decimal quantity	Volume in composite sample, dm ³	Flow rate, m ³ h ⁻¹	Mixing proportions, decimal quantity	Volume in composite sample, dm ³
1. Enrichment tailings of BCP	2137	0.755	3.77	2137	0.653	3.26	2137	0.792	3.96
2. Acid effluents neutralization sludge of BCSP	133	0.047	0.23	574	0.175	0.88	-	-	-
3. Industrial effluents from									
- a machinery and repair plant	180	0.064	0.32	180	0.055	0.27	180	0.067	0.33
- a non-ferrous metal processing plant	6	0.002	0.01	6	0.002	0.01	6	0.002	0.01
- a copper electrolysis shop	38	0.014	0.07	38	0.012	0.06	38	0.014	0.07
- a charge preparation shop	119	0.042	0.21	119	0.036	0.18	119	0.044	0.22
- an oxygen production plant	219	0.077	0.39	219	0.067	0.34	219	0.081	0.41
Total pulp:	2832	1	5	3273	1	5	2699	1	5

Thus, under laboratory conditions, it was simulated 3 circulating water samples entering the water intake well of the tailings dam after combined storage of acid effluents neutralization sludge with enrichment tailings according to scheme A1:

$$1_{CW} - 3_{CW} = 0.44 \times ST (1_{ST} - 3_{ST}) + 0.14 \times HASS + 0.12 \times ISS + 0.30 \times DW, \quad (1)$$

where: ST - a composite sample of enrichment tailings and neutralization sludge; HASS - water sample from the hydraulic ash sluicing system; ISS - industrial storm sewer; DW - drainage water.

Similarly, considering the increase in productivity for acid effluents of BCSP, circulating water was modelled according to scheme A2:

$$4_{CW} - 6_{CW} = 0.48 \times ST (4_{ST} - 6_{ST}) + 0.13 \times HASS + 0.11 \times ISS + 0.28 \times DW \quad (2)$$

Modelling of circulating water according to scheme B

In the tailings dam, clarified water from the pulp of composite samples obtained according to schemes B is mixed with clarified water from section for acid

effluents neutralization sludge and section for hydraulic ash sluicing system (HASS) of BCHPP as well as with industrial storm sewage (ISS) effluents from BCP and BCSP facilities and drainage water (DW) in the proportions indicated in Table 2.

Thus, under laboratory conditions, it was simulated 6 circulating water samples entering the water intake well of the tailings dam after separate storage of acid effluents neutralization sludge and enrichment tailings according to scheme B1 (Eq. 3) or scheme B2 (Eq. 4):

$$7_{CW} - 9_{CW} = 0.42 \times T (1_T - 3_T) + 0.02 \times S (1_S - 3_S) + 0.14 \times HASS + 0.12 \times ISS + 0.30 \times DW \quad (3)$$

$$10_{CW} - 12_{CW} = 0.40 \times T (1_T - 3_T) + 0.08 \times S (1_S - 3_S) + 0.13 \times HASS + 0.11 \times ISS + 0.28 \times DW \quad (4)$$

Determination of circulating water composition

Samples of circulating water (model mixtures $1_{CW} - 12_{CW}$) were allowed to settle, then they were filtered through a 45 nm filter (before analysis) to remove small suspended particles, and components characterizing its ionic-molecular composition were determined in clarified water: cations Na^+ , K^+ , Ca^{2+} , Mg^{2+} , anions Cl^- , SO_4^{2-} , NO_2^- , NO_3^- , metals Mo, Al, Cu, Zn, Ni, As, Pb, Cd, Co, Fe, Si,

Table 2. Modelling of circulating water obtained with combined or separate waste storage in the tailings dam.

Industrial wastewater name	Scheme A1 with samples $1_{ST} - 3_{ST}$		Scheme A2 with samples $4_{ST} - 6_{ST}$		Scheme B1 with samples $1_S - 3_S, 1_T - 3_T$		Scheme B2 with samples $1_S - 3_S, 1_T - 3_T$	
	Flow rate, $m^3 h^{-1}$	Mixing proportions, decimal quantity	Flow rate, $m^3 h^{-1}$	Mixing proportions, decimal quantity	Flow rate, $m^3 h^{-1}$	Mixing proportions, decimal quantity	Flow rate, $m^3 h^{-1}$	Mixing proportions, decimal quantity
1. Clarified water pulp of composite samples (ST or T)	2832	0.44	3273	0.48	2699	0.42	2699	0.40
2. Acid effluents neutralization sludge of BCSP (S)	-	-	-	-	133	0.02	574	0.08
3. Clarified water of hydraulic ash sluicing system of BCHPP (HASS)	873	0.14	873	0.13	873	0.14	873	0.13
4. Industrial storm sewage effluents from BCP and BCSP (ISS)	747	0.12	747	0.11	747	0.12	747	0.11
5. Drainage water (DW)	1941	0.30	1941	0.28	1941	0.30	1941	0.28
Total:	6392	1	6833	1	6392	1	6833	1

as well as pH value, suspended solids, permanganate oxidation, chemical oxygen demand (COD).

To measure the pH value and electrical conductivity of solutions, the “Expert-001” device was used, equipped with appropriate electrodes and a temperature compensator.

Cation concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) (in laboratory at “Azimut Geology” LLP). For a few cations, microwave plasma atomic emission spectrometry (MP-AES) was used (in engineering laboratory “Physical and chemical research methods” at the Karaganda Buketov University).

Since currently in the Republic of Kazakhstan there are no valid Interstate Standards-and/or Measurement Procedures for measuring the concentration of metals in aqueous solutions using atomic emission spectrometers with microwave plasma excitation so it was used methods based on data from scientific periodicals and

Measurement Procedure developed at the Lomonosov Moscow State University by a partner laboratory of Agilent Technologies Inc [12 - 14]. Both MP- and ICP-AES are sensitive to matrix effects and give better results when using calibration samples close in composition to those under study [17 - 19]. When performing analysis in the engineering laboratory “Physical and chemical research methods”, multicomponent calibration mixtures containing relatively high concentrations of sulfate ions and sodium cations were used to calibrate the device. It brings the calibration mixture composition closer to the analytes composition and allows achieving the necessary parameters of analysis accuracy.

RESULTS AND DISCUSSION

In Table 3, there are presented the composition of circulating water samples ($1_{cw} - 12_{cw}$), which was determined at the chemical-analytical laboratory of

Table 3. Characteristics of circulating water supplied to the Balkhash Concentrator Plant under different conditions of waste storage.

Defined indicator	Content (mg dm ⁻³) in the sample or indicator value							
	in the case of combined waste storage							
	according to Scheme A1				according to Scheme A2			
	1_{cw}	2_{cw}	3_{cw}	average	4_{cw}	5_{cw}	6_{cw}	average
Chlorides Cl ⁻	1400	1294	1312	1335	1276	1241	1276	1264
Sulphates SO ₄ ²⁻	3434	3290	3362	3362	3170	3122	3070	3120
Nitrates NO ₃ ⁻	1.29	1.30	1.40	1.33	1.64	1.47	1.68	1.60
Nitrites NO ₂ ⁻	0.40	0.05	0.10	0.18	0.20	0.05	0.10	0.12
Calcium Ca ²⁺	421.8	412.8	403.3	412.6	422.8	433.8	409.8	422.1
Magnesium Mg ²⁺	216.1	210.8	205.4	210.8	200.4	197.8	200.6	199.6
Sodium Na ⁺	1480	1431	1357	1423	1306	1291	1273	1290
Potassium K ⁺	108.7	103.5	99.6	103.9	98.0	95.0	92.8	95.3
Oxidizability*	2.52	2.08	2.08	2.23	2.32	1.92	2.48	2.24
pH value	7.98	7.97	7.97	7.97	7.84	7.67	6.62	7.38
Suspended solids	105.8	156.8	185.7	149.4	115.6	138.5	119.8	124.6
COD**	220	176	140.8	178.9	299.2	176	264	246.4
Silicon Si	4.68	5.16	4.99	4.94	5.28	5.25	5.03	5.19
Aluminum Al	0.07	0.28	0.10	0.15	0.09	0.08	0.06	0.08
Arsenic As	0.03	0.07	0.11	0.07	0.40	0.56	0.34	0.43
Cadmium Cd	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001
Cobalt Co	0.018	0.013	0.015	0.02	0.028	0.032	0.026	0.03
Copper Cu	0.21	0.237	0.206	0.22	0.177	0.195	0.171	0.18
Iron Fe	0.09	2.05	2.54	1.56	1.49	1.98	1.37	1.61
Molybdenum Mo	0.23	0.229	0.238	0.23	0.21	0.206	0.203	0.21
Nickel Ni	0.12	0.128	0.092	0.11	0.157	0.169	0.146	0.16
Lead Pb	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Zinc Zn	0.08	0.08	0.09	0.08	0.18	0.22	0.15	0.18

Table 3. Characteristics of circulating water supplied to the *Balkhash* Concentrator Plant under different conditions of waste storage - *continued*.

Defined indicator	in the case of separate waste storage							
	according to Scheme B1				according to Scheme B2			
	7 _{CW}	8 _{CW}	9 _{CW}	average	10 _{CW}	11 _{CW}	12 _{CW}	average
Chlorides Cl ⁻	1578	1225	1225	1342	1542	1436	1489	1489
Sulphates SO ₄ ²⁻	3530	3554	3554	3546	3386	3674	3602	3554
Nitrates NO ₃ ⁻	5.81	5.76	6.89	6.15	5.87	6.20	7.35	6.47
Nitrites NO ₂ ⁻	0.10	0.10	0.10	0.10	0.07	0.10	0.10	0.09
Calcium Ca ²⁺	441	417.3	436	431.4	447.8	435.3	449.5	444.2
Magnesium Mg ²⁺	229.5	215.0	223.9	222.8	219.4	217.4	225.1	220.6
Sodium Na ⁺	1638	1466	1555	1553	1503	1528	1562	1531
Potassium K ⁺	120.8	111.8	113.4	115.3	113	111.1	113.7	112.6
Oxidizability*	1.92	2.08	1.92	1.97	3.36	2.88	3.52	3.25
pH value	7.84	7.78	7.81	7.81	7.24	7.22	7.20	7.22
Suspended solids	123.4	122.4	121.5	122.4	174.3	162	166.5	167.6
COD**	264	211.2	228.8	243.7	176	255.2	184.8	205.3
Silicon Si	3.70	3.63	3.73	3.69	4.22	4.00	3.92	4.05
Aluminum Al	0.14	0.12	0.10	0.12	0.25	0.28	0.22	0.25
Arsenic As	0.42	0.37	0.26	0.35	1.27	1.43	1.54	1.41
Cadmium Cd	0.0002	0.0003	0.0002	0.0002	0.0003	0.0003	0.0004	0.0003
Cobalt Co	0.015	0.019	0.014	0.016	0.030	0.030	0.034	0.031
Copper Cu	0.624	0.587	0.292	0.500	1.242	1.616	1.489	1.45
Iron Fe	3.34	2.94	1.11	2.46	7.93	11.33	11.2	10.15
Molybdenum Mo	0.254	0.233	0.241	0.24	0.232	0.216	0.236	0.23
Nickel Ni	0.978	0.935	0.938	0.950	3.858	3.311	3.763	3.640
Lead Pb	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Zinc Zn	0.17	0.16	0.14	0.16	0.33	0.34	0.35	0.34

Note: * - oxidizability by permanganate method, ** COD - chemical oxygen demand.

“Azimut Geology” LLP according to the standard procedure.

As can be seen from the analysis results, the main number of electrolytes in circulating water are sodium, magnesium, and calcium cations, and, to a much lesser extent, potassium. Anions are mainly sulfate- and chloride-ions (Table 3). The main technogenic source of sulfate-ions are effluents of BCSP containing sulfuric acid in their composition. This acid is largely neutralized by lime materials; however, the neutralized sludge still enters the tailings dam in a relatively acidic state (pH = 6 - 7).

In the case of separate waste storage, there is a slight increase in the content of SO₄²⁻ anions (with combined storage 3362 and 3121 mg dm⁻³; with separate storage 3546 and 3554 mg dm⁻³) and Ca²⁺ cations (with combined storage 412 and 422 mg dm⁻³; with separate storage 431 and 444 mg dm⁻³).

At the same time, in all model mixtures of recycled water obtained according to schemes A, there was a

significant decrease in the concentrations of copper, arsenic, iron, zinc, cadmium, nickel (Table 3), which can be explained by the binding of corresponding cations into insoluble compounds (hydroxides, hydroxocarbonates, etc.). This is a positive moment for the flotation enrichment process, since studies have shown that an increased content of copper, iron, zinc ions in circulating water leads to a decrease in the quality of commercial copper-molybdenum concentrates [1].

When waste stored separately, the liquid phase of neutralization sludge remains acidic and cations of iron, copper, several other elements, as well as arsenic compounds continue to be in dissolved form in it. Therefore, in case of the circulating water formation according to scheme B by mixing flows before use, higher concentrations of these elements are observed in them.

Based on the CaSO₄ solubility product, when sulfate ions concentration is about 3120 - 3554 mg dm⁻³, the

calcium content in the solution cannot significantly exceed 130 mg dm^{-3} . Consequently, most of the calcium is not in the form of free ions in the solution, but forms calcium sulfate microparticles. The process of calcium sulfate crystal formation will be accompanied by occlusion (co-precipitation) of other cations, whose sulfates are soluble (Cu^{2+} , Zn^{2+} , etc.), and, accordingly, a decrease in their concentration in solution, if appropriate interaction time and pH values (in the weakly alkaline region) are provided.

The achievement of the required pH value is carried out in this case by mixing acidic wastewater from BCSP with weakly alkaline wastewater from BCP and BCHPP. This leads to mutual deneutralization of the flows and, as a result, promotes the binding of cations during occlusion.

Circulating water obtained with storage of neutralization sludge and enrichment tailings according to both schemes are characterized by neutral pH values and do not differ significantly in this indicator (Table 3). The average pH values are 7.97 and 7.38 when waste stored together and 7.81 and 7.21 when they stored separately. As can be seen, circulating water obtained according to schemes A2 and B2 has lower pH values, since it is formed considering the higher productivity for the acid effluents neutralization site of BCSP.

With long-term storage of clarified water, its pH value changes towards an increase in alkalinity. Experiments to study the influence of the settling time (i.e., the duration of its storage in storage tanks) on the change in pH circulating water were carried out in the engineering laboratory "Physical and chemical research methods" Karaganda Buketov University. For the study, two samples with a volume of 2 dm^3 were used, prepared according to scheme A (Eq. 5) and scheme B (Eq. 6) in the following proportions:

$$13_{\text{CW}} = 0.96 \times \text{ST} (7_{\text{ST}}) + 0.26 \times \text{HASS} + 0.22 \times \text{ISS} + 0.56 \times \text{DW} \quad (5)$$

$$14_{\text{CW}} = 0.80 \times \text{T} (4_{\text{T}}) + 0.16 \times \text{S} (4_{\text{S}}) + 0.26 \times \text{HASS} + 0.22 \times \text{ISS} + 0.56 \times \text{DW} \quad (6)$$

The results of pH measurements for 24 hours at certain intervals are shown in Table 4.

During combined waste storage, a lower content of arsenic was noted (with combined storage 0.07 and 0.43 mg dm^{-3} ; with separate storage 0.35 and 1.41 mg dm^{-3}) in circulating water. In an aqueous medium and with access to atmospheric oxygen, arsenic is oxidized to an arsenate ion, which binds to practically insoluble arsenates, mainly magnesium arsenate (its solubility in a neutral medium is $0.0016 \text{ g per } 0.1 \text{ dm}^3$). In an acidic environment, the solubility of arsenates increases, so the pH values about 7 - 8 achieved for circulating water have a good effect on its quality and environmental situation. At the same time, the combined waste storage according to scheme A provides a greater reduction in the concentration of arsenic due to the possibility of co-crystallization with gypsum and other poorly soluble compounds.

It should also be noted that the separate storage of acid effluents neutralization sludge leads to localization in the tailings dam section of an environmental hazard potential source, which is to a greater extent their liquid part returned to the technological needs of BCP in which dissolved arsenic content is 61.95 mg dm^{-3} . In the solid part, formed during storage, arsenic content is 0.158 mg kg^{-1} (0.01 %).

Based on laboratory analyzes of circulating water obtained as a result of modeling the waste storage conditions in the tailings dam show that the ionic-molecular composition of circulating water obtained with combined storage of enrichment tailings from the Balkhash Concentrator Plant and acid effluents neutralization sludge from the Balkhash Copper Smelter Plant is more preferable for use as a medium in processes of copper ore flotation. According to many parameters that determine and affect the quality of flotation, the circulating water obtained with Scheme A has an

Table 4. Results of pH measurements for samples 13_{CW} and 14_{CW} .

Sample name	pH value					
	5 min	8 min	10 min	13 min	60 min	24 h
13_{CW}	7.58	7.77	7.87	7.98	8.11	8.70
14_{CW}	7.67	7.90	7.96	8.11	8.17	8.60

advantage. As the most important parameter for the flotation process, a 2-fold decrease in the concentration of dissolved copper in the circulating water can be distinguished in comparison with the technology of separate waste storage according to scheme B.

Studies have shown that in case of combined waste storage, after they are mixed in the tail collector, chemical and physico-chemical processes occur that contribute to the removal of a few pollutants from circulating water. So, in all model mixtures of circulating water obtained according to scheme A, there was a significant decrease in the concentrations of not only copper ions, but also ions of arsenic, iron, zinc, cadmium, and nickel compared to their content in model mixtures of circulating water obtained according to scheme B. That can be explained by the binding of these ions into insoluble compounds.

CONCLUSIONS

Water management is the crucial aspect of every mineral processing plant. To achieve cleaner production mining companies must implement technological solutions on water reuse in internal water circuits.

As shown by our simulation experiments, for the circulating water conditioning at the Balkhash Concentrator Plant, it is recommended to use a technology that involves preliminary mixing enrichment tailings with acid effluents neutralization sludge (wastewater from the Balkhash Copper Smelter Plant) in the tail collector and their combined storage in the tailings dam. This technology allows to influence ionic-molecular composition of circulating water and 2-fold decrease the concentrations of copper, iron, zinc, cadmium, and nickel ions, and arsenic in it. Moreover, the organization of the fullest possible use of all industrial effluents of the Balkhash Mining and Processing Combine in its circulating water supply system will reduce significantly negative impact on the environment.

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