Reutilization of neutralization sludge formed during the processing of mining enterprises acidic industrial waters

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Abstract
It was established that neutralization sludges formed during the processing of acidic industrial waste waters of mining enterprises are aluminate and hydroxide. The structure, chemical composition and grain size distribution, fractal dimension, structural and rheological properties of the sludge were studied. Two methods of sludge reutilization were developed: low-temperature and high-temperature cementation with further use of the products obtained in the production of asphalt, construction and filling materials or in the manufacture of building ceramics and Portland cement clinker.
Key words: INDUSTRIAL WATER, NEUTRALIZATION SLUDGE, REUTILIZATION METHODS, CHEMICAL AND GRAIN SIZE DISTRIBUTION, FRACTAL DIMENSION

The number of papers devoted to reutilization and use of industrial neutralization sludge produced in the processing of acidic industrial waste waters is very limited [1, 3, 5-7, 10] It should be noted that the reutilization of these sludge is impossible without physical-chemical analysis of their composition and properties, which are determined by the matrix of industrial water, pH medium, temperature, the amount of reactants added and etc. It should be taken into account that during the neutralization not only metal hydroxides, but also basic salts can be formed. Iron hydroxide (III) is formed in the first stage of neutralization and it is capable of surface adsorption of other metal ions. In the course of time at the completion of the process of iron hydroxide precipitation, the formation of double hydroxides with subsequent precipitation or co-precipitation of basic salts of the respective metals is possible. Thus, co-precipitated neutralization sludge is mainly mechanical mixture of hydroxides and basic salts.

The research objective is to study neutralization of sludge generated during the acidic industrial waste waters processing of mining enterprises and to establish their operational properties and possible reutilization.

Materials and methods

The study was conducted with the use of neutralization sludge of JSC "Gaiskiy GOK» and CJSC «Buribaevsky GOK" and standardized test solutions, the composition of which is close to the actual neutralization sludges. The methods of atomic absorption analysis, potentiometry, photocolorimetry, x-ray phase (radiographic) analysis, thermogravimetric differential-scanning calorimetry were used in the study. The precipitation kinetics was evaluated by changes in the volume of precipitating solid phase during some period of time. The sludge density was determined by densitometeric method, water ratio - by gravimetric method.

Research results and their discussion

Results of study of kinetics of suspension precipitation obtained in the neutralization of acidic mine waters are shown in Fig. 1.

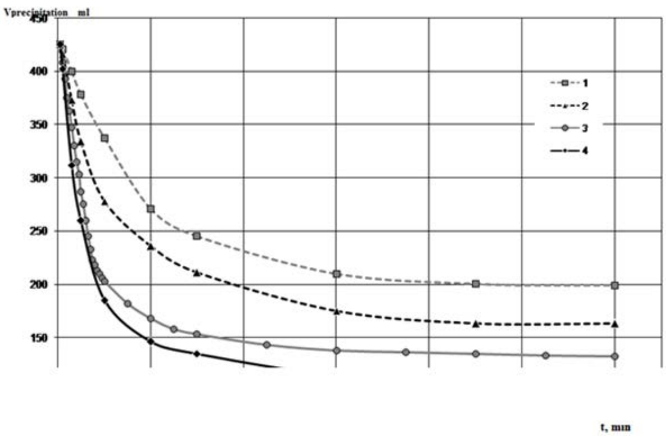
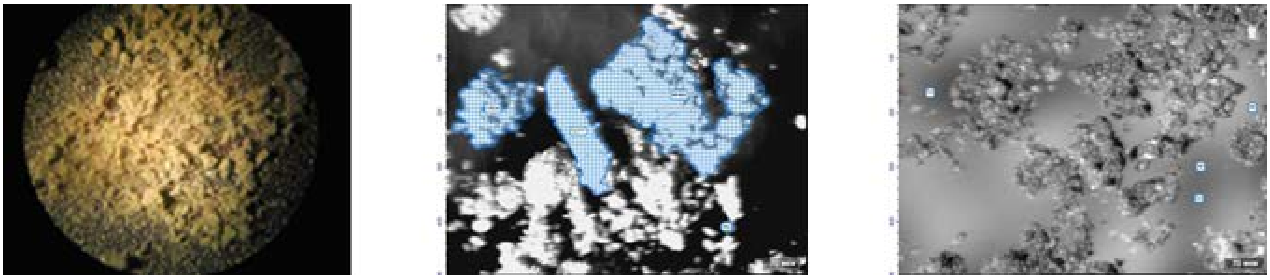


Figure 1. Kinetic curves of suspensions precipitation: 1 – $Fe(OH)_3$, 2 - $Zn(OH)_2$, 4 – $Cu(OH)_2$ of neutralized single-component model systems; 3 - of the acidic underspoil water of JSC "Gaiskiy GOK"

Analysis of the kinetic curves has shown that during the first 7 minutes the deposition rate is almost unchangeable, the initial section of the deposition curve is rectilinear. Accordingly, the formed particles of disperse phase have a sufficiently large sizes and approximately the same shape. After 10 minutes 76.3% of suspended mixture are precipitated. Rapid precipitation is due to the presence of such solutions coagulators-ions in the matrix as Fe^{3+}, SO_4^{2-}.

The liquid phase of industrial waste waters of concentration plant prior to the neutralization process is often a heterogeneous system containing suspended matters and colloids (degree of dispersion 10^6 mm^{-1}) in addition to true dissolved substances. Except ore and metal with minerals, the obtained precipitate contains clay particles formed as a result of concentrating repartition of host rocks; grains with fineness of 0.001-0.0002 mm are more than 95 %.

Microscopic analysis of the structural components of the precipitation formed by the natural deposition (Fig. 2 a, b) and in the neutralization process of the acidic underspoil water of JSC "Gaikiy GOK" (Fig. 2c) has confirmed that deposition of precipitates are uniform grains with fineness 1.0-0.2 microns (more than 95% of precipitate); neutralization sludges are homogenous mass with an average particle size of 70 microns which have a greater strength.



a) b) c)

Figure 2. Structure of solid phase acidic industrial waste waters:
a - the clay component formed during mechanical deposition; b - ore (dark) and non-metallic (light) mechanical sludge particles; c - the neutralization sludge

Neutralization sludges as chemical deposition products have high surface activity and dispersibility. The high degree of dispersion gives a stable coagulant structure to the sludges. Studing of this structure allows characterizing the degree of homogeneity, dispersion and properties of the resulting neutralization precipitation such as formability, strength, moisture content etc., as well as selecting the most comprehensive method for their processing.

The sludges are the closest analogues of highly plastic clay, so the physical and chemical processes of sludge formation are mainly identical to the formation of clay structure and are associated with water exposure. The signs of their commonality include the presence in sludges and clays of the smallest particles, the presence of the water adsorption and high plasticity [8].

As shown above, the iron hydroxide (III) is formed at the initially step of industrial waste waters neutralization. When precipitation the coagulated particles of iron hydroxide (III) form so-called chains, on which surface colloidal impurities are adsorbed. The pores filled with water are formed during the process of constructing chain structures jointed in rings. Consequently the precipitate contains a large amount of water retained by particles of iron hydroxide (III) [4]. The peculiarity of the investigated sludge as analogues of highly plastic clay is their flexibility, which determines the possibility of their use in the production of various building materials.

The basis of clay and sludge plasticity is their high absorption capacity and a high degree of self-organization. The research results [2] show an identity mechanism of clay and sludge plasticity and their topological similarity.

Despite the differences in chemical composition of clays and sludges the structural-rheological properties of the latter is much higher than that of clay. This is due to size factor of the sludge particles and big amount of adsorption-bound water.

Mineral sludges by definition of M. M. Sychev [9] are concentrated solutions of inorganic polymers formed in the hydrolytic polymerization process of low-concentrated non-equilibrium suspensions – industrial wastewater. The technology of their production allows attributing sludge to the nanodispersion materials of technogenic origin. The sludges have a spatial coordination of the dispersed phase due to coupling of colloidal particles and crystals through the water layer.

Chemical composition of the investigated sludge is shown in Table 1.

The true density of sludge 1 is equal to 4.592 kg/m^3, sludge 2 – 3.959 kg/m^3.

In accordance with the chemical composition, the sludges are classified as aluminate and hydroxide: these sludges contain predominantly oxides of di- and trivalent metals – Al_2O_3, Fe_2O_3, Cr_2O_3, NiO, ZnO, CuO.

Table 1. Chemical composition of the sludge neutralization of JSC "Gaiskiy GOK" (sludge 1) and CJSC "Buribaevsky GOK (sludge 2)

Oxides	Sludge 1			Oxides	Sludge 2		
	Sample No 1	Sample No 2	Sample No3		Sample No 1	Sample No 2	Sample No 3
CuO, %	1.45	1.40	1.37	CuO, %	1.33	1.44	1.29
ZnO, %	1.08	1.16	1.05	ZnO, %	0.12	0.08	0.11
Fe_2O_3, %	63.05	64.72	66.18	Fe_2O_3, %	58.03	58.17	52.22
MnO_2, %	0.027	0.020	0.020	MnO_2, %	1.15	1.12	1.23
CaO, %	0.68	0.79	0.72	CaO, %	0.41	0.43	0.42
MgO, %	0.48	0.45	0.36	MgO, %	0.95	0.86	0.92
K_2O, %	0.22	0.21	0.29	K_2O, %	0.66	0.59	0.56
Na_2O, %	0.14	0.11	0.18	Na_2O, %	0.05	0.11	0.13
Al_2O_3, %	29.10	33.71	31.03	Al_2O_3, %	41.06	35.30	41.24
SiO_2, %	0.02	0.01	0.01	SiO_2, %	0.01	0.01	0.01

Grain size distribution of neutralization sludge of the acidic underspoil water of JSC "Gaiskiy GOK" is presented in Table 2.

Evaluating the structure-rheological properties of the sludges the plastic consistency (velocity of the suspension flowing from the hopper), plastic strength (when immersing the cone to the solution), the rate of solid particles falling in the low-concentration suspension (settling time), the amount of sedimentation sludge were studied. The results obtained are shown in Table. 3.

It has been established that the positive effect on the rheological properties of the neutralization sludge have the following oxides Al_2O_3, Fe_2O_3, RO ($CuO+ZnO+MnO_2$), which are present in the sludge in the form of amorphous hydroxides. They greatly increase the adsorptive capacity of the particles, thereby enhancing the ductility. The higher rheological characteristics of neutralization sludge of the acidic underspoil water of JSC "Gaiskiy GOK" are due to a significant content of zinc oxide in its composition. Higher volume of this sludge precipitation also proves its higher ductility and therefore, the sludge self-organization degree.

Peculiarity and difference of the sludge materials obtained by grinding is their high dispersion. Material with such dispersion has a fractal structure, which determines the features of contact interactions of solid phase particles in the sludge. With the increase of fractal dimension the cohesiveness ability of sludge particles increases, i. e., the adsorption-bound water layer is enlarged, which positively affects the properties of sludge.

Table 2. Grain size distribution of neutralization sludge of the acidic underspoil water of JSC "Gaiskiy GOK" (sludge 1) and CJSC "Buribaevsky GOK" (sludge 2)

Grain size class, mm	Sample No1				Sample No2			
	Yield		Total yield		Yield		Total yield	
	g	%	top	bottom	g	%	top	bottom
	Grain size distribution of neutralization sludge of the acidic underspoil water of JSC "Gaiskiy GOK" (sludge 1)							
+ 25	-	-	-	-	0.16	0.067	0.067	98.35
-25+16	-	-	-	-	0.172	0.12	0.187	98.28
-16+1	0.1162	0.08	0.08	98.57	0.26	0.17	0.357	98.16

-1+0.63	0.3926	0.26	0.34	98.49	1.192	0.79	1.147	97.99
-0.63+0.4	1.7723	1.18	1.52	98.23	5.214	3.47	4.617	97.2
-0.4+0.315	5.182	3.45	4.97	97.05	10.295	6.86	11.48	93.73
-0.315+0.2	18.081	12.05	17.02	93.6	23.192	15.46	26.94	96.87
-0.2+0.16	3.228	2.15	19.17	81.55	3.275	2.18	29.12	71.41
-0.16+01	36.5824	24.39	43.56	79.4	44.118	29.41	58.53	69.23
-01+0063	37.147	24.76	68.32	55.01	27.654	18.44	76.97	39.82
-0063+005	42.107	28.07	96.39	30.25	12.09	8.06	85.03	21.38
-005+0	3.277	2.18	98.57	2.18	19.901	13.27	98.3	13.32
TOTAL	148	98.57			147.6	98.358		
Smple weight	M_{init} = 150 g				M_{init} = 150 g			
Grain size class, mm	Sample No1				Sample No2			
	Grain size distribution of neutralization sludge of the acidic underspoil water of CJSC "Buribaevsky GOK" (sludge 2)							
+ 25	0.1762	0.25	0.25	99.5	0.12	0.08	0.08	94.12
-25+16	0.6220	0.44	0.69	99.25	0.088	0.06	0.14	94.04
-16+1	2.16115	1.34	2.23	98.81	0.224	0.15	0.29	93.98
-1+063	11.6445	8.32	10.55	97.27	1.0783	0.72	1.01	93.83
-063+04	10.31855	7.37	17.92	88.95	2.2881	1.53	2.54	93.11
-04+0315	6.4115	4.58	22.5	81.58	4.28345	2.86	5.4	91.58
-0315+02	10.8924	7.78	30.28	77.0	13.4159	8.94	14.34	88.72
-02+016	1.974	1.41	31.69	69.22	3.15615	2.1	16.44	79.78
-016+01	19.2778	3.77	45.46	67.81	31.2853	20.86	37.3	77.68
-01+0063	34.7222	24.8	70.26	54.04	52.3323	34.89	72.19	56.82
-0063+005	34.8237	24.87	95.13	29.24	29.6382	19.76	91.95	21.93
-005+0	6.1152	4.37	99.5	4.37	3.2621	2.17	94.12	2.17
TOTAL	139.14	99.5			142	94.12		
Sample weight	m_{init} = 140 g				M_{init} = 150 g			
Grain size class, mm	Sample No3				Sample No3			
	Yield		Total yield		Yield		Total yield	
	g	%	top	bottom	g	%	top	bottom
	Grain size distribution of neutralization sludge of the acidic underspoil water							
	JSC "Gaiskiy GOK" (sludge 1)				CJSC "Buribaevsky GOK" (sludge 2)			
+ 25	-	-	-	-	0.2042	0.14	0.14	99.23
-25+16	0.175	0.12	0.12	99.3	0.1853	0.12	0.26	99.09
-16+1	0.414	0.28	0.4	99.18	1.016	0.68	0.94	98.97
-1+0.63	2.518	1.68	2.08	98.9	7.0155	4.68	5.62	98.29
-0.63+0.4	9.16	6.11	8.19	97.22	10.543	7.03	12.65	93.61
-0.4+0.315	11.603	7.74	15.93	91.11	7.112	4.74	17.39	86.58
-0.315+0.2	27.355	18.24	34.17	83.37	14.004	9.34	26.73	81.84
-0.2+0.16	4.864	3.24	37.41	65.13	2.218	1.48	28.21	72.5
-0.16+01	41.744	27.83	65.24	61.89	23.912	15.94	44.15	71.02

-01+0063	26.451	17.64	82.88	34.06	42.208	28.14	72.29	55.08
-0063+005	10.983	7.32	90.2	16.42	38.396	25.60	97.89	26.94
-005+0	13.647	9.1	99.3	91	2.003	1.34	99.23	1.34
TOTAL	149	99.3			148.82	99.23		
Sample weight	M_{init} = 150g				M_{init} = 150 g			

Table 3. The averaged rheological properties of the neutralization sludge of the acidic underspoil water

Rheological properties of the neutralization precipitation	CJSC "Buribaevsky GOK"	JSC "Gaiskiy GOK"
Plasticity indicator	1048.76	1165.28
Time of suspension flowing from the hopper, s	20.84	4.89
Ratio of precipitation volume to the volume of initial suspension	1.21	1.13
Suspension density, g/sm^3	0.77	0.88
Elasticity indicator	1.19	1.30
Threshold of structure formation, %	17.04	9.01
Plastic strength , 10^{-2} mPa	0.31	0.52

The fractal dimension of the investigated sludge was calculated using the program «Shlam» based on their grain size distribution (Table 2). The program «Shlam» on the basis of two-dimensional and three-dimensional diagrams of the chemical composition of sludge and sludge simulated aggregate models during the study allowed establishing a link between the chemical composition, structural and rheological properties of hydrolytic sludge and properties obtained based on these materials, as well as determining the most effective area of neutralization sludge application.

When calculating the fractal dimension the range of variation percentage of the particle amount of this diameter were selected as restriction, and as the optimality criterion the total squared deviation from the average percentage of particles of the given diameter was used. The results obtained are shown in Fig. 3 and Fig.4.

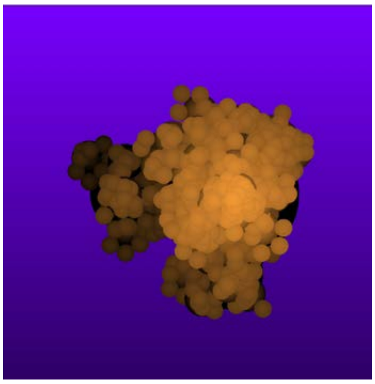


Figure 3. Aggregate model of neutralization sludge of JSC “Gaiskiy GOK”

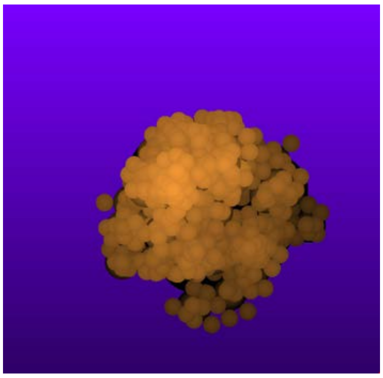


Figure 4. Aggregate model of neutralization sludge of CJSC “Buribaevsky GOK”

Analysis of the aggregate models data showed:

- “Gaiskiy GOK” sludges form precipitates with a higher aggregate dimension, their nonuniform structure have more points of contact and adhesion between itself and therefore characterized by a high threshold of structure formation and plastic strength, but a smaller value of plasticity index that ultimately determines the improved binding properties of building mixtures with additives of this material.

- “Buribaevsky GOK” sludges form a precipitation in the form of regular, uniform aggregates characterized by the large indicator of elasticity and plasticity, lower threshold of structure formation and plastic strength index that allow us to attribute these sludges to additives with high degree of plasticity and better transportability, pumpability with the possibility of their use in drilling fluids.

On the basis of conducted researches the following sludge reutilization methods were developed.

The first method involves the sludge drying and its use as a mineral powder in the composition of asphalt concrete mixtures in the construction of roads or other building and filling mixes (low-temperature carburizing).

The second method provides the involvement of the sludge into the clay mass composition in the production of building ceramics, or as a part of the raw material mixture for the production of Portland cement clinker (high cementation).

A study of low-temperature carburizing method has shown that after the removal of moisture by drying or by reacting with calcium oxide sludge analyzed according to its physical and chemical indicators meets the requirements for mineral powders that are recommended for all types of asphalt concrete mixtures.

The method of high-temperature cementing sludge is based on the application of the wet sludge in the composition of clay raw materials in the production of building ceramics. To justify the sludge use in this method, the behavior of air-dried hydroxides of heavy metals and co-precipitated with iron hydroxide at temperature influence has been investigated.

Thermogravimetric studies have shown that during high temperature impact the heavy metal hydroxides form oxides (except the basic copper salt) having substantially lower solubility in water and co-precipitated ones with ferric hydroxide and metal hydroxides are insoluble ferrites (in a temperature range from 400 ^{o}C to 650 ^{o}C). Therefore, high temperature cementation in a matrix of clay raw material is a very effective recycling process of sludges containing heavy metal hydroxides.

The calculation of raw mixture composition has shown that the tested sludges can be advantageously used as a raw iron component in the manufacture of Portland cement clinker (Table 4).

Table 4. Chemical composition of clinker raw ferrous component

The chemical composition of raw material mixture and clinker,%									
Components	Amount	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Sum
Limestone	77.99	34.83	0.16	0.08	0.16	39.13	3.52	0.05	78.70
Clay	20.26	1.88	12.71	2.96	0.79	0.58	0.59	0.04	19.76
Sludge	1.74	0.11	0.00	0.51	1.10	0.01	0.01	0.00	1.75
Raw material mixture composition		36.82	12.87	3.55	2.04	39.72	4.12	0.09	99.21
Clinker composition		0.00	20.36	5.62	3.23	62.86	6.53	0.14	98.74
Minerals		C3S	C2S	C3A	C4AF	Sum			
		58.84	14.10	9.40	9.83	92.16			

Conclusion

Investigation of the structure, chemical and grain size distribution composition, fractal dimension, structural and rheological properties of sludge neutralization produced in the processing of acidic industrial waste waters of the mining enterprises helped to develop two methods of sludge reutilization.

The first method (low-temperature carburizing) involves drying sludge and its use as a mineral powder in the composition of asphalt concrete mixtures in the construction of roads or other building and filling mixtures.

The second method (high-cementation) envisages the involvement of sludge into the clay mass in the production of building ceramics or in the composition of raw mixture for the production of Portland cement clinker.

Use of the program «Shlam» on the basis of two-dimensional and three-dimensional diagrams of the chemical composition and simulated aggregation models of sludge allows establishing a link between the chemical composition, structural and rheological properties of the hydrolytic sludges and the properties obtained based on these materials, as well as determining the effectiveness of their reutilization by these methods.

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