

ТЕХНОЛОГИИ ПЕРЕРАБОТКИ И УТИЛИЗАЦИИ ТЕХНОГЕННЫХ ОБРАЗОВАНИЙ И ОТХОДОВ

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METHODS OF SULFATE REMOVAL FROM MINING WASTE WATERS: OVERVIEW

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Abstract

Industrial waste waters rich in heavy metal ions and sulfates are a common phenomenon caused by oxidation of sulfide ore bodies and associated waste. Oxidized products enter a water body leading to a greater number of metal ions, a higher concentration of dissolved salts and a lower pH thus affecting the quality of water. As the environmental impact of sulfates is less detrimental than that of dissolved metals or acidity, the sulfate control has received little attention in many regulatory jurisdictions. It should be noted that the literature on sulfate removal from industrial waste waters is relatively sparse. However, a number of techniques are available to lower the concentration of dissolved ions, including sulfate ions. The sulfate control levels are based on the maximum permissible concentration (MPC) of approximately 100 mg/l for fisheries and on the secondary drinking water recommendations of approximately 500 mg/l. Methods of sulfate removal from industrial waste waters can be of two types: removal through semi-permeable membranes; removal by salt precipitation through ion exchange; permeable reactive barrier; biological recovery or insoluble mineral precipitates. This article offers an overview of the main sulfate removal options for industrial waste waters, as well as a feasibility study comparing the available techniques. The feasibility study suggests that among the techniques available today, biological methods and methods involving chemical reagents offer the most advanced options. An effective low-cost pre-treatment option for sulfates includes lime treatment, which is relevant if the sulfate concentration exceeds 2,000 mg/l. The most suitable option for sulfate removal will be dictated by site-specific conditions of a particular mining operation.

Keywords: removal options, acid mine waters, sulfate ions, reverse osmosis, chemical method, ion exchange, bio-removal.

Introduction

Wastewater treatment with the extraction of valuable components has received much attention in recent years due to it is one of the most important tasks of rational use of natural resources in the mining enterprises activity. It is economically important for the wastewater treatment technology to include the receipt of demanded products and easily recyclable sludges.

The main difficulty is to treat large volumes of technogenic wastewaters. This leads to high economic and material costs in the implementation of various treatment schemes. In addition, wastewater is a complex multi-component system, containing

dissolved metals with high sulfate content, colloids, solid suspended substances of both inorganic and organic origin [1].

Technogenic waste waters are classified in three types: mine, quarry and subsurface. The contamination of technogenic waste waters is primarily due to sulfide minerals oxidation because of their instability in hypergenic conditions. Technogenic waste waters are the most polluted.

Although the environmental impact of sulfate ions is comparably lower than other dissolved pollutants, the sulfate control and mine water conditioning have been given little attention in mining enterprises.

The situation has changed due to reformations in Russian environmental legislation. These changes significantly increase the fees for discharges exceed-

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ing the limits, in 25 times instead of 5 to date. The factor of 25 is used in respect of emissions and discharges in excess of established permit limits on emissions and discharges, as well as ultimately permitted emissions (UPE) и normatively permitted discharges (NPD) – if limits are not installed [2,3]. Rivers are water receivers of cleaned waters from mining enterprises. In addition, in recent years, almost all the rivers have been transferred to the category of fishery water reservoirs. It leads to increase the demands on the water cleaning including salt composition.

This review will assess the options available for sulfate removal from mine, subsurface and other types of technogenic waters for conditioning and discuss an economic and technical comparison made between the available technologies.

The article presents the review of existing sulfate removal options for technogenic waste waters.

Technogenic waste waters (TWW) of mining enterprises are classified into: open pit, mine, and subsurface. Open pit acidic waters are formed during construction and operation of pits. Construction and exploitation of mines leads to the formation of mine acidic waters. Subsurface acidic waters contain dissolved minerals leached from sulfide components of the off-grade and off-balance ores, overburden and enclosing rocks. The chemical composition of acidic technogenic waste waters depends on sulfide mineralization of ores such as ferrous, non-ferrous and rare earth metals.

It is known that the following characteristics are common for these waters: low activity values of hydrogen ions ($\text{pH} = 1,5 - 4,5$), high concentrations of sulfur-containing salts of macro- and microelements, high values of redox potential (Eh) [6, 7].

According to their chemical composition, technogenic waste waters do not meet water quality standards of fishery water bodies, including the standard of maximum permissible concentration of harmful substances in waters of fishery water bodies. There are presented three of the main indicators:

- high mineralization (up to 3 g/l), therefore, about 2 million tons of mineral salts are discharged annually into water bodies and rivers;

- pollution with suspended solids (90-110 mg/l), which causes water bodies siltation;

- the increased heavy metal ions content (in 1,5-15 times).

The oxidation processes of sulfide minerals proceed through a complex multistage mechanism, which leads to an increase in acidity and water saturation with heavy metals cations and sulfate anions [27, 46, 48].

Nevertheless, it is found that technogenic waste

waters with high sulfate concentration have a corrosive effect and a high scale potential as well [39].

The article presents the scientific and technical literature review of Russian and foreign authors and the comparative analysis of available sulfate removal technologies from technogenic waste waters.

Sulfate removal methods can be divided into physical, physicochemical, chemical and biological [30, 32, 41–43, 50, 52].

Physical methods

Physical methods include reverse osmosis and its modifications, filtration. These methods have not previously been used for desalination of acidic technogenic waste waters of mining enterprises, but recently the Russian's largest mining and metallurgical company "UMMC – holding" is studying the possibility of using these methods in their enterprises.

The technogenic waste water removal technology based on reverse osmosis which relies on a semi-permeable membrane separating a strong solution and a dilute solution. In this technology, an external hydraulic pressure allows to overcome osmotic pressure, thus forcing water through the membrane receiving two streams [8].

Reverse osmosis is designed for the removal of up to 99% of dissolved organic and inorganic substances, including sulfates.

The advantages of reverse osmosis are: firstly, it does not require using of a traditional reagent-precipitator, such as lime; secondly, receiving water with pollutants concentrations ten times lower than the requirements of maximum permissible concentrations (MPC) for fishery water bodies, thirdly, the possibility of using dilute solution as recycled water in the enterprise production cycle [28, 31, 37, 38, 47].

The disadvantages include:

1. the necessity in pre-removal of suspended particles on micro filters with a pore size of less than 5 microns;

2. low dilute output at each stage and, as a consequence, constructing a series of membrane elements to implement the process and reach 60-75% level of the initial water flow;

3. the limitation of the minimum concentrate volume, which is determined both the apparatus hydrodynamics, and the solubility of salts removed from the water. It should be stressed that scale forming salts can be deposited on the membranes surface and lead to a decrease in productivity, membrane elements corrosion and membrane surface fouling by mineral deposits of insoluble salts (alkaline earth metals carbonates, calcium sulfate in the gypsum form);

4. application of antiscaling agents for prevention of crystalline salts deposit formation on the membrane surface;

5. the problem of brine disposal, which is formed during the division of technogenic waste water into two streams and containing pollutants in concentrations significantly exceeding the water quality standards of fishery water bodies, including standards of MPC of harmful substances in waters of fishery water bodies [9, 10].

The following method for sulfate removal is filtration, which is used to extract fine-dispersed substances at the stage of deep removal (post-treatment) of technogenic waste waters after physicochemical or biological treatment, consisting in the separation of suspensions using porous partitions or granular layers, which separate the dispersed phase and pass the liquid.

The following filtering processes are used in the practice of technogenic waste water treatment [25]:

- filtration through filter walls;
- filtration through granular layers;
- microfiltration.

The advantages of filtering are:

1. obtaining filtrate that meets the requirements for the content of solid insoluble substances;
2. complete passage of filtrate through the filter screen in comparison with reverse osmosis;
3. the applicability of the filtration as one of the stages in technological water removal process.

The disadvantages include:

1. the process duration;
2. obtaining filtrate with high metal and sulfate content.

Physicochemical methods

Physicochemical methods include electro dialysis, ion exchange [33].

In electro dialysis an external direct current and a stack of alternating cation and anion selective membranes are applied to extract the salts from technogenic waste water. In this electro-membrane process anions and cations are attracted to the anode and to the cathode. Cations and anions are concentrated between cation-impermeable barrier and anion-impermeable membranes.

Advantages of electro dialysis are, 1. this process does not require additional reagents for its implementation; 2. processability: the electro dialyzers provide ease of maintenance and reliability in operation; 3. low power consumption; 4. the system is not sensitive to effluent temperature or pH; 5. the recyclability of extracted components to the production; 6. Capital costs are reduced due to lower working pressures.

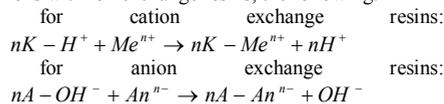
Disadvantages: 1, the concentration polarization, leading to the salts deposition on the membrane surface, which leads to lower treatment efficiency; 2, the low intensity.

Periodic (approximately every 15 minutes) switching of the current polarity greatly improves electro dialysis. The reverse electro dialysis reduces fouling and facilitates membrane regeneration.

Nevertheless, insufficient pre-treatment may occur a large amount of calcium sulfate deposition on the electrodes [11].

The ion exchange method (IEM) allows to clean technogenic waste waters by means of absorption of positive or negative ions of "pollution" by ion exchange resins in exchange for an equivalent amount of hydrogen protons and hydroxyl anions of ionite [12, 33].

The basic equations of ion exchange, schematically describing the reaction of the interaction of ions with ion exchange resins, the following:



Thus, by means of ion exchange, technogenic waste water is cleaned from heavy metal ions (Zn^{2+} , Cr^{3+} , Hg^{2+} , Ni^{2+} , Cu^{2+}), including alkaline earth metal ions (Mg^{2+} , Ca^{2+}), ammonia salts and anions (Cl^- , SO_4^{2-} , CNS^- , CN^- etc.).

The ion exchange technology can be used to treat solutions with sulfate up to 2000 mg/L.

The advantage of the IEM allows to achieve the content of pollutants to the maximum permissible concentration.

The advantage of the ion exchange method: it has been designed to reduce gypsum levels in effluent thereby achieving the maximum permissible concentration of total dissolved solids and reducing corrosion potential.

The disadvantages of ion exchange are: 1. significant consumption of aggressive reagents for regeneration; 2. the operating costs, increasing in proportion to the salinity of technogenic waste waters; 3. high costs of recycling solutions.

Chemical methods

Chemical methods include lime treatment, barium-containing and aluminum-containing reagents.

Lime treatment is a traditional technology for technogenic waste water treatment plants, based on neutralization with the production of complex precipitation containing metal hydroxides and calcium sulfate in the form of gypsum [34, 36, 44, 49]. This

method provides only partial cleaning of technogenic waste waters from sulfate ions. It should be stressed that the concentration of sulfates in the cleaned water exceeds the MPC of the fishery water bodies value by 15–20 times.

The advantages of lime treatment is the simplicity of the cleaning process and reagent availability.

The disadvantages include: 1. the insufficient degree of cleaning of acid technogenic waste waters from heavy metal ions; 2. a large amount of multi-component sludge, 3. the necessity of an additional cleaning stage from trace heavy metal ions and sulfates.

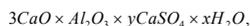
Barium salts such as $BaCl_2$, $BaCO_3$ are used to reduce sulfates concentration in technogenic waste waters up to 100 mg/L [13, 40, 53]. Barium hydroxide $Ba(OH)_2$ [14] is proposed as an complex reagent because of its good solubility and strong alkaline reaction. According to stoichiometry the sulfate concentration from 380 to 75 mg/dm³ can be reduced with 0.54 g $Ba(OH)_2$.

The advantages are: 1. all barium-containing reagents can remove sulfates from waste waters from high levels to within regulatory standards; 2. acidic waste waters can be treated directly with BaS and $Ba(OH)_2$; 3. during the cleaning process valuable products are created.

The main disadvantages are that barium compounds are very toxic and the high cost of barium containing reagents.

Sulfate removal through the precipitation of ettringite can be realized by means of aluminum-containing reagents.

The mechanism of the chemical process include many stages. The first stages is the interaction of aluminate anion in an alkaline medium with calcium ions producing various hydrated forms of calcium aluminate. This compound interacts with sulfate ions [19, 20, 21, 22, 23, 24]. The product of this reaction is the complex sulfate containing precipitate in the form of calcium hydro-sulfur-aluminate (CHSA):



$$\text{где } y = 1 \div 3, \quad x = 12 \div 32$$

The resulting calcium hydro-sulfur-aluminate precipitations are insoluble and non-toxic compounds. The undoubted advantage of this method is the receiving valuable product which can be used as a raw material in the building materials production [4]. The disadvantage of the method is the high pH value of water (above 12.0), which requires carbonization stage to reduce the pH of cleaned water.

Biological methods

Anaerobic conditions allow to remove sulfate from technogenic waste waters as stable sulfide containing precipitates. The process of sulfate reduction is brought about by strictly anaerobic bacteria of two genera: *Desulfovibrio* spp. (five species) and *Desulfotomaculum* spp. (three types). These organisms use reductive sulfur compounds (sulfate, sulfite, etc.) in a respiratory metabolism generating hydrogen sulfide [5]. Suitable conditions for the implementation of a sulfate reduction system can be made in flooded underground mine workings and open pits.

Biological sulfate reduction include oxidation of organic substances generally short chain organic acids and the destruction of phosphates, nitrates, ammonium ions. As a result, hydrogen sulfide reacts with dissolved metal ions, forming insoluble sulfide salts [15, 26, 29, 35, 45, 51].

This process requires a bioreactor [16, 17, 18], with maintaining correct conditions to sustain bacterial activity. To improve the efficiency of treatment, it is necessary to strictly control the flow rate of cleaned technogenic waste water.

Dill et al. investigated the practical application of bioreactors in the current production. As a result, it was found that the content of sulfate ions decreased from 3000 mg/l to 250 mg/l for 70 h [16].

The advantages of the biotechnological method are: 1. the process does not require reagents for its implementation; 2. reducing the concentration of heavy metal ions and sulfates up to the MPC requirements.

The disadvantages of biological treatment are: 1. duration; 2. complexity of hardware design; 3. control for the temperature and flow rate of cleaned technogenic waste water, as well as the addition of reducing substances.

Evaluation of treatment options for sulfate removal

The criteria for implementation one of the sulfate removal options depend on the ability of the technology to remove sufficient sulfates in a given time, the effectiveness and economic parameters of technogenic waste water treatment from polluting ions, discharge of the treated water meets the water quality standards of water bodies of fishery importance.

Table 1 presents data on the economic evaluation of capital and operating costs for the treatment of 1000 m³ of technogenic waste waters per day. It is established that the use of reverse osmosis is characterized by the highest operating costs for water cleaning in comparison with reagent methods.

In conclusion, it should be noted that currently the most popular are reagent-free methods, namely membrane and ion exchange technologies. However, the use of these methods to clean large volumes of technogenic waste waters is constrained by technical and economic indicators: high capital and operating costs and not fully solved environmental problems associated with waste disposal.

Based on the fact that, at present, almost all mining and processing enterprises use the traditional and economical method of cleaning (liming) with an increase in pH of water to 9-11, the reagent sulfate removal technology is suitable by deposition in the ettringite composition ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), proposed in 1999 by J. R. Smith and the SAVMIN process [50] (Fig. 1).

The process involves three successive stages: at the first stage heavy metal ions removal in the form of hydroxides by adding lime to pH 12. At the second stage the removal of gypsum by fractional crystallization and the addition of aluminum hydroxide to form insoluble ettringite. At the final stage, to reduce the pH, carbon dioxide is added and pure calcium carbonate is precipitated. The ettringite may be further disposed or dissolved in the sulfuric acid for the regeneration of aluminum hydroxide. The technology was successfully tested in South Africa, during which 500 m³ of water with an initial sulfate concentration of 800 mg/l was recycled, further reduced to values of less than 200 mg/l. [3]

Despite the attractiveness of the technology, today its use is not economically justified. Consequently, it is important to adapt the technology for mining enterprises.

Attempt at such adaptation was made by "EvoSintez" Ltd in the enterprise of "Mednogorsky copper-sulfur combine" Ltd located in the Orenburg region, the treatment technology of technogenic waste waters, suggests in our opinion the following steps.

At the first step, the retention of the liming stage, which consists in simultaneously and effectively reducing the content of heavy metal ions and sulfate ions. The content of sulfate ions after first stage varies between 1,300 and 1,100 mg/l.

In the second stage, wastewater is treated to obtain a stable high-sulfate containing form of ettringite suitable for use in the construction industry.

One of the limiting factors in the stable type of ettringite formation is the hydrogen index maintenance at the level of 12.5 units during the entire process of deep sulfate removal to values less than 100 mg/l.

Future research will include the calculation of the thermodynamic conditions for the ettringite formation with high and low sulfate content; determination the stability limits of the various ettringite forms; the thermodynamic calculations of the formation ettringite compounds containing various anions and the kinetics of ettringite formation.

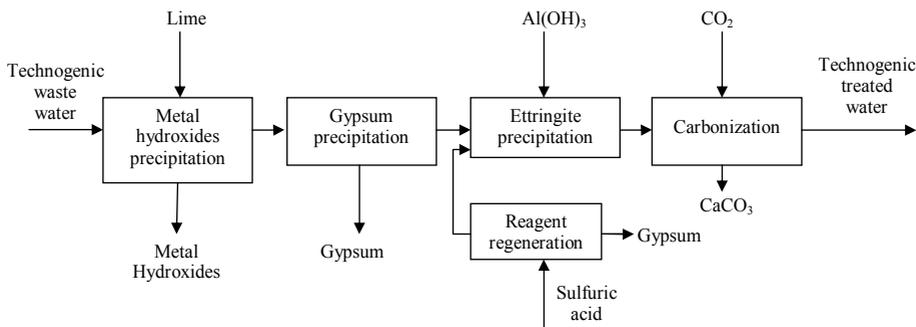


Figure 1. The SAVMIN-process

Table 1

Comparative analysis of existing sulfate removal options for technogenic waste waters and with reagents of “Evrosintez” Ltd

Parameter	Options											
	Reverse osmosis		Filtration		Reagent options						Bioreactor	
					Limestone/Lime		BaS		Reagents of “Evrosintez” Ltd			
Pretreatment	Yes		Yes		No		No		No		Yes	
Feed water sulfate limits	Any		Any		Any		Any		Any		Any	
Sulfate removal, %	> 99		> 95		50		> 98		> 99		> 90	
Brine production	Yes		Yes		No		No		No		No	
Sludge production	low		moderate-high		Low-moderate		Low-moderate		moderate-high		Low-moderate	
Monitoring	Low-moderate		moderate-high		moderate-high		high		moderate-high		moderate-high	
Maintenance	high		high		low		low		moderate		moderate	
Capital cost, RUB/per10 ³ m ³ /day	£ 0.46 M	37.8	£ 0.14 M	11,5	£ 0.13 M	10,2	£ 0.25 M	19.8		10,2	£ 0.18 M	14.3
Operating cost, RUB/m ²	£0.49	40.3	£0.15	11.9	£0.13	10.2	£0.27	21.4		50	£0.2	15.8
Advantages	drinking water quality		drinking water quality		- trace metal removal; - very cheap		- utilization of H ₂ S and CO ₂ ; - recycling of expensive BaS		- sulfate removal up to 100 mg/l;		trace metal recovery; recycling of H ₂ S and CO ₂ ;	
Disadvantages	- scaling problems; - short membrane life - production of sludges		- scaling problems; - production of sludges - limited sulfate removal		- limited sulfate removal; - production of sludges		- little trace metal removal; - production of sludges		- production of sludges		- cost of C + energy source; - production of sludges	
Improvements	Not suitable for large water volumes		-		- sludge recycling		- sludge recycling		- sludge recycling		- - sludge recycling; -specific design required	

Conclusions

Sulfate removal from technogenic wastewaters is considered to be of secondary importance compared to removal of metals and acidity. As such, it is worth noting that methods for sulfate removal up to 100 mg/dm³ have not yet been implemented in industrial practice, because of technical and economic acceptability.

Various options for sulfate removal were compared in economic and technical aspects. The presented comparison of sulfate removal options

proved that most of them are not suitable for wastewater disposal of mining enterprises. Electrofiltration methods are considered to be more attractive to treat technogenic waste waters up to 1000 m³/day for economic reasons. However, reagent methods are more realistic for implementation because of the presence of capacitive structures at mining enterprises for collection and accumulation of huge water volumes. Nevertheless, some limitations of reagent methods are worth noting, i.e. relatively inexpensive technical reagents and optimization of the process kinetic.

References

- Federal Law No. 219-FZ dated July 21, 2014, "On amendments to the Federal Law "On Environmental Protection" and certain legislative acts of the Russian Federation". (In Russ.)
- Environmental impact charge: Calculation and collection rules, enacted by the decree No. 255 of the RF Government dated March 3, 2017. (In Russ.)
- Masloubov V.A. Vigdergauz V.E. et al. Techniques for reducing the concentration of sulfates in mining wastewater. *Vestnik Kolskogo nauchnogo tsentra RAN* [Bulletin of Kolsky Science Centre of the Russian Academy of Sciences]. 1/2017 (9), pp. 99-115. (In Russ.)
- Abdrakhmanova R.N., Orekhova N.N., Nefediev A.P. Understanding how to apply a double-action reagent to remove sulfates from the water and obtain an additional product. *Sovremennye problemy kompleksnoy pererabotki trudnoobogatimyykh rud i tekhnogennogo syrya (Plaksinskie chteniya – 2017): materialy Mezhdunarod. Nauch. Konf.* [Current problems in the comprehensive processing of complex ores and manmade materials (Plaksin Readings-2017): Proceedings of the International Science Conference], Krasnoyarsk, 12-15 September 2017. Krasnoyarsk: Siberian Federal University, 2017, 452 p. (In Russ.)
- Chappelle, F.M. 1993 Groundwater Microbiology and Geochemistry. Prentice-Hall.
- Emlin E.F. *Tekhnogenez kolchedannykh mestorozhdeniy Urala* [Technogenesis of the pyrite deposits of the Urals]. Sverdlovsk: Publishing House of the Ural University, 1991. (In Russ.)
- Shulenina Z.M., Plaul P. Acid drainage. *Global Studies: Encyclopedia*. Moscow: Raduga, 2003, pp. 440-442. (In Russ.)
- Dytnerky Yu.I. Reverse osmosis and ultrafiltration. Moscow: Khimiya, 1978, 352 p. (In Russ.)
- Kucera J. Reverse Osmosis. Industrial applications and processes. 2010, p. 393.
- Pulles W., Juby G.J.G., and Busby R.W. 1992 Development of the Slurry Precipitation and Recycle Reverse Osmosis Technology for desalination technogenic waste waters. *Water Science & Technology*, 25, 25 pp.
- Juby G.J.G. and Pulles W. 1990. Evaluation of Electrodialysis reversal for desalination of blackish mine water. WRC Report 179/1/90.
- Helfferich F. 1962 Ion Exchange. McGraw-Hill, San Francisco: 624 pp.
- Adlem C.J.L. 1997 Treatment of sulfate-rich effluents with the barium sulfide process. MSc. thesis. University of Pretoria, South Africa.
- Adlem C.J.L., Maree J.P., and Pleiss P.Du. 1991. Treatment of sulfate-rich mining effluents with the Barium Hydroxide process and recovery of valuable by-products. In: 4th International Mine Water association Congress, Ljubljana (Slovenia) – Portsachach (Austria), September 1991, pp. 211–221.
- Frank Yu.A., Lushnikov S.V. Biochemical potential of sulfate-reducing bacteria. *Ekologiya i promyshlennost* [Ecology and industry], 2006, no. 1, pp. 10-13. (In Russ.)
- Dill S., Du Preez L., Graff M. and Maree J. 1994 Biological sulfate removal from acid mine drainage utilizing producer gas as carbon and energy source. 5th International Mine Water Congress, September 1994, pp. 631–641.
- Henze M., Herremoes P., La Cour-Jansen., Arvan E. *Ochistka stochnykh vod. Biologicheskije i khimicheskije protsessy* [Wastewater treatment. Biological and chemical processes]. Moscow: Mir, 2004. (In Russ.)
- Morozova K.M. Biological wastewater treatment systems: Design principles. *Vodosnabzhenie i sanitarnaya tekhnika* [Water supply and sanitary engineering], 2009, no. 1. (In Russ.)
- Kim M.P., Molodchik G.L. *Sposob ochistki stochnykh vod ot sulfat-ionov* [Technique for removing sulfate-ions from wastewater]. Patent RF, no. 2236384. Applied: 2003. Published: 2004. (In Russ.)
- Kim M.P., Molodchik G.L., Agapov A.E., Azimov B.V., Navitny A.M. *Sposob ochistki stochnykh vod ot sulfat-ionov* [Technique for removing sulfate-ions from wastewater]. Patent RF, no. 2322398. Applied: 2006. Published: 2008. (In Russ.)
- Kim M.P., Molodchik G.L., Agapov A.E., Azimov B.V., Navitny A.M. *Sposob ochistki stochnykh vod ot sulfat-ionov* [Technique for removing sulfate-ions from wastewater]. Patent RF, no. 2323164. Applied: 2006. Published: 2008. (In Russ.)
- Grishin V.P., Makarov O.V., Nekryachenko S.G. Pat. *Sposob ochistki stochnykh vod ot sulfat-ionov* [Technique for removing sulfate-ions from wastewater]. Patent RF, no. 2559489. Applied: 2014. Published: 2015. (In Russ.)
- Kim M.P., Molodchik G.L. *Sposob ochistki stochnykh vod ot sulfat-ionov* [Technique for removing sulfate-ions from wastewater]. Patent RF, no. 2233802. Applied: 2003. Published: 2004. (In Russ.)
- Nurkeev S.S., Ozerov A.I., Kospanov M.M., Musina U.Sh. *Sposob ochistki stochnykh vod ot sulfat-ionov* [Technique for removing sulfate-ions from wastewater]. Patent USSR, no. 1724597 A1. Applied: 1989. Published: 1992. (In Russ.)
- Buchanan J. 1987 Basics of filtration. *Water Sewage & Effluent*. September 1987; 35-36.
- Chappelle F.M. 1993 Groundwater Microbiology and Geochemistry. Prentice-Hall.
- Cravotta C.A. III 1994 Secondary iron-sulfate minerals as sources of sulfate and acidity. In: *Environmental Geochemistry of Sulfate Oxidation* (eds. C.N. Alpers and D.W. Blowes). American Chemical Society Symposium Series, 550. 1994. 345-364.
- Du Pleiss G.H. and Swartz J.A. 1992 Tubular Reverse Osmosis treatment of Secunda mine water: a pilot plant investigation. *Water Science Technology*, 25, 193-201.
- Du Preez L.A., Maree J.P., and Jackson-Moss C.A. 1992 Biological sulfate removal from industrial effluents. *Environmental Technology*, 13: 875-882.
- Eckenfelder W.W. 1989 *Industrial Water Pollution Control*. McGraw Hill, 400 p.
- Eriksson P. 1988 Nanofiltration extends the range of membrane filtration. *Environmental Progress*, 7: 58-62.
- Everitt D.J., Du Plessis J. and Gussman H.W. (1994) The removal of salt from underground technogenic waste waters. *Mining Environmental Management*, March 1994: 12-14.
- Feng D., Aldrich C., and Tan H. 2000. Treatment of acid mine water by use of metal precipitation and ion exchange. *Minerals Engineering*, 13(6), 623-642.
- Geldenhuis A.J., Maree J.P., de Beer M. and Hlabela P. 2001 An integrated limestone/lime process for partial sulfate removal. *Proceedings of Environmentally Responsible Mining in South*

- Africa, September 2001. CSIR, Pretoria, South Africa.
35. Gould W.D., Bechard G. and Lortie L. 1994 The nature and role of microorganisms in mine drainage. In: Environmental Geochemistry of Mine Waste, (eds: J.L.Jambor and D.W. Blowes), 185-199, MAC.
 36. Gussman H.W. and Nagy P. 1993 The development and operation of the GYPCIX pilot plant, JCI MPRL, Johannesburg, SA, July 1993.
 37. Harries R.C. 1985 A field trial of Seeded Reverse Osmosis for desalination of a scaling type mine water. Desalination, 56: 227-236.
 38. Juby G.J.G. 1989 Membrane desalination of mine water. WISA Conference. March 1989.
 39. Kleinmann R.L.P. and Pacelli R.R. 1991 Biogeochemistry of acid mine drainage. Mining, Engineering, 33, 300-6.
 40. Kun L.E. 1972 A report on the reduction of the sulfate content of acid mine drainage by precipitation with barium carbonate. Anglo American Research Laboratories. D/3W/1.
 41. Lorax 2003 A review of sulfate treatment. Report to INAP by Lorax consultants. Electronic document, INAP website.
 42. Marree J.P. 1989 Sulfate removal from Industrial effluents. PhD thesis. University of the Orange Free State.
 43. Maree J.P., Bosman D.J. and Jenkins G.R. 1989 Chemical removal of sulfate, calcium and metals from mining and power station effluents. Water Sewage and Effluent, 9: 10-25.
 44. Marree J.P. and Du Plessis P. 1994 Neutralization of acid mine water with calcium carbonate. Water Science & Technology, 29: 285-296.
 45. Marree J.P., Hulse G., Dods D. and Schutte C.E. 1991 Pilot plant studies on biological sulfate removal. Water Pollution Research and Control, part 3. CSIR.
 46. Nordstrom D.K. 1982 Aqueous pyrite oxidation and the consequent formation of secondary minerals. In: Acid Sulfate Weathering, 37-56. Soil Science Society of America.
 47. Pulles W., Juby G.J.G., and Busby R.W. 1992 Development of the Slurry precipitation and Recycle Reverse Osmosis Technology for desalinating technogenic waste waters. Water Science & Technology, 25, 25 p.
 48. Robins R.G. et al. 1997 Chemical, physical and biological interaction at the Berkerley Pit, Butte, Montana. Tailings and Mine Waste 97. 529-541. Balkema, Rotterdam.
 49. Robertson A.M., Everett D., Du Plessis P. 1993 Sulfate removal by GYPCIX process following lime treatment. In: SUPERFUND XIV Conference, 30/11-2/12/93, Washington USA.
 50. Smit J.P. 1999 The cleaning of polluted mine water. Proceedings of the International Symposium on Mine Water & Environment for the 21st Century, Seville, Spain.
 51. Trudinger A., Chambers L.A., and Smith J.W. 1985 Low temperature sulfate reduction: biological versus abiological. Canadian Journal of Earth Sciences, 22, 1910-1918.
 52. Trusler G.E., Edwards R.I. Brouckaert C.J., and Buckley C.A. 1988 The chemical removal of sulfates. Proceedings of the 5th National Meeting of the South African Institute of Chemical Engineers, Pretoria, W3-0-W3-11.
 53. Wilsenbach I. 1986 Cost estimate for barium sulfate reduction. Internal report of the Division of Water Technology, CSIR, 620/2616/6.
 54. Abdrakhmanova R.N., Nefedjev A.P., Abdrakhmanov R.N. Overview of methods for removing sulfates from mine waters. *Actual problems of mining*, 2018, no. 5, pp. 38–43. (In Russ.)

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ОБЗОР МЕТОДОВ УДАЛЕНИЯ СУЛЬФАТОВ ИЗ ТЕХНОГЕННЫХ ВОД ГОРНЫХ ПРЕДПРИЯТИЙ

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Аннотация

Техногенные сточные воды богаты ионами и сульфатами тяжелых металлов, являются обычным явлением, связанным с окислением сульфидов добытых рудных тел и обработанных отходов. Окисленные

продукты попадают в водный организм, влияющий на качество воды за счет увеличения содержания металлов, концентрации растворенных солей и снижения потенциала водорода. Воздействие сульфата на окружающую среду ниже, чем растворенные металлы

или кислотность, и контроль над сульфатом получил мало внимания во многих регулирующих юрисдикциях. Следует отметить, что литература по удалению сульфатов из техногенных сточных вод сравнительно небольшая, хотя используется и разработано несколько технологий для снижения концентрации растворенных ионов, включая сульфаты. Уровни контроля сульфатов основаны на требованиях предельно допустимых концентраций (ПДК) приблизительно 100 мг/л для промышленных водоемов и рекомендаций по вторичной питьевой воде приблизительно 500 мг/л. Методы удаления сульфатов из техногенных сточных вод подразделяются на два типа: удаление через полупроницаемое мембранное разделение; удаление путем осаждения соли посредством ионного обмена; проницаемый реактивный барьер; биологическое восстановление или образование нерастворимого минерального осадка. В статье представлен об-

зор основных вариантов удаления сульфатов для техногенных сточных вод, экономическое и техническое сравнение доступных технологий. На основе продемонстрированного сравнения и экономических выгод наиболее перспективными на сегодняшний день являются биологический и реагентные технологии. Эффективным вариантом недорогой и предварительной обработки для сульфата является обработка извести при условии, что концентрация сульфата превышает 2000 мг/л. Наиболее подходящий вариант для удаления сульфата будет определяться специфическими для конкретного участка условиями для конкретной операции добычи.

Ключевые слова: методы очистки, кислые рудничные воды, сульфат-ионы, обратный осмос, реагентный способ, ионный обмен, биоочистка.

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