Justification the Possibility of Sludge Storage Use for Liquid Wastes from the Potash Industry as Settling Ponds

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Abstract

In process of the enrichment of potash ores during the potassium chloride production by flotation, liquid wastes are formed - a mixture of clay-salt slurries and industrial wastewater; the utilization of such mixtures is a complex environmental and technological problem.

In Russia, the main method of disposal of liquid waste from potash producing industrial units is wastes release into sludge storage basins with further return of the clarified water into the production cycle or injection of clarified liquid waste into underground horizons.

Performed analysis of the facilities operation at Uralkali's mine departments, calculated water and material balances of the sludge storage facilities, data of the suspended solids sedimentation efficiency and the water mineralization reduction made it possible to consider such facilities not only as environment protection units, but also as waste treatment facilities. Calculations of the speed and time of fine clay particles sedimentation, changes in water mineralization in the sedimentation pond depth due to the density and thermal stratification, allowed to develop the technology of the facility liquid waste treatment and to determine its main structural features with the possibility to release the part of slightly mineralized water into the water body during the pre-flood period.

Key words: potash production industry, liquid waste, brine, sludge storage unit, sediment pond

Introduction

The Verkhnekamskoye mine field of potassium-magnesium salts is one of the world's largest deposits of potassium salts. Commercial development of the field began in the 30s of the XX century. The mining and processing of ores are accompanied by the formation of substantial waste volumes – solid halite waste and liquid clay-salt slimes, whereas the utilization and processing of such wastes is one of the complex environmental and technological problems. Taking into account the composition of the feedstock containing 23 – 27% KCl, the process of one ton of potassium chloride production generates formation of 0.1 - 0.5 tons of clay-salt sludge. The solution of ecological problems regarding potash mine fields development is of current concern, both in Russia and abroad.

Data on methods of potash production facilities liquid wastes disposal and handling were analyzed. The results demonstrated that following main methods were used worldwide (Baturin,2012, Goldberg, 1994) :

- release of sludge containing brine into ocean and sea bodies (Canada, Brasil, Great Britain);
- regulated release of brine into rivers (Germany, France, Russia);
- pumping into underground absorbing strata (Germany, Belorussia, Canada)

- storage in special sludge accumulation units (Russia).

The determination of options for the liquid waste disposal (diffused discharge into rivers, underground discharge by injection wells and by brine and sludge storage units) depends on the natural hydrological and geological - hydrogeological conditions, so for each mine field the method and/or a set of methods will be different. It is most advisable to use an integrated approach to the problem while using several options or an options' combination.

In Russia, despite the existing experience of liquid wastes processing, the main method of such waste disposal is still the storage in sludge storage units with the return of clarified water into the production cycle or injection of clarified liquid waste into underground absorbing horizons. Sludge storage unit is usually considered as a hydraulic engineering structure for waste accumulation.

Basing on the analysis of the operation of sludge collectors at PJSC Uralkali (four production complexes in Berezniki and three production complexes in Solikamsk) and the processes occurring in these collectors, the purpose of this work was to substantiate the possibility of using sludge collectors as waste treatment facilities (sedimentation ponds).

Characteristics of the research objects

Liquid waste

During flotation processing of Verkhnekamsky mine field potash ores the specific yield of clay-salt sludge per one ton of finished product is 0,5- 0,6 m^3/t, including 0,32 -0,35 t/t of the solid particles phase.

Solid particles phase characteristics

Mineral content density: 2,2 ÷2,4 t/m^3.
Particle-size distribution:

Size, mm	>0,1	0,1-0,063	0,063-0,045	< 0,045
Size frequencies, %	2 – 6	2 - 4	1,0 -2,5	70- 89

Clay sludges are of the fine nature (mass content of <0,045 mm particles is 70-80%); by the capillary forces action they have the moisture-binding capacity and create difficulties in their processing and disposal.

Solid particles phase chemical composition:

- mass content of KCl (expressed in terms of solid part), % - 10,0 -12;
- mass content of NaCl (expressed in terms of solid part), % - 18,0 -20;
- mass content of insoluble residue, % - 68 - 72,0.

Liquid phase characteristics

Liquid phase density: 1,22 t/m^3.

Liquid phase chemical composition:

- mass content of KCl, % - 5,7 -6,0
- mass content of NaCl, % - 15,3 -20;
- dry residue, % - 21,0 -26;
- water, % - 79,0 – 74,0

After mixing of clay-salt slurries with industrial effluents the Liquid/Solid ratio can change from 10 to 14 and doesn't exceed the value of 35. The average chemical composition of liquid waste entering the sludge storage unit is shown in the table 1.

The presented data demonstrate that liquid effluents are characterized by a high content of suspended solid particles and mineral impurities.

Sludge storage unit

The structure of the facilities for mining industry wastes storage usually includes systems of waste hydraulic transportation, their hydraulic packing, sludge storage unit and clarified brine circulation system. Sludge storage unit is usually a structure of bulk plain-type or bulk ravine-type. The construction consists of a bed-base,

Table 1 *– average chemical composition of liquid waste entering the sludge storage unit*

Component	Measure unit	Content		Concentration change, (± %)
		Waste water	Clarified waste water (recycled brine)	
Suspended matter	mg/L	60125	9,1	- 99,98
Dry residue at t=105°C	mg/L	351900	191492,0	- 45,6
Chlorides	mg/L	192800	104667,0	-46,0
Ammonia nitrogen	mg/L	215,28	484,38	+55,0
K-cation	mg/L	59800	27908,	-53,2
Ca- cation	mg/L	2060	2287,0	+11,0
Mg- cation	mg/L	684	511,0	-25,3
Na – cation	mg/L	79300	48500	-50,5
Sulphate- ion	mg/L	2690	2403,0	-10,7

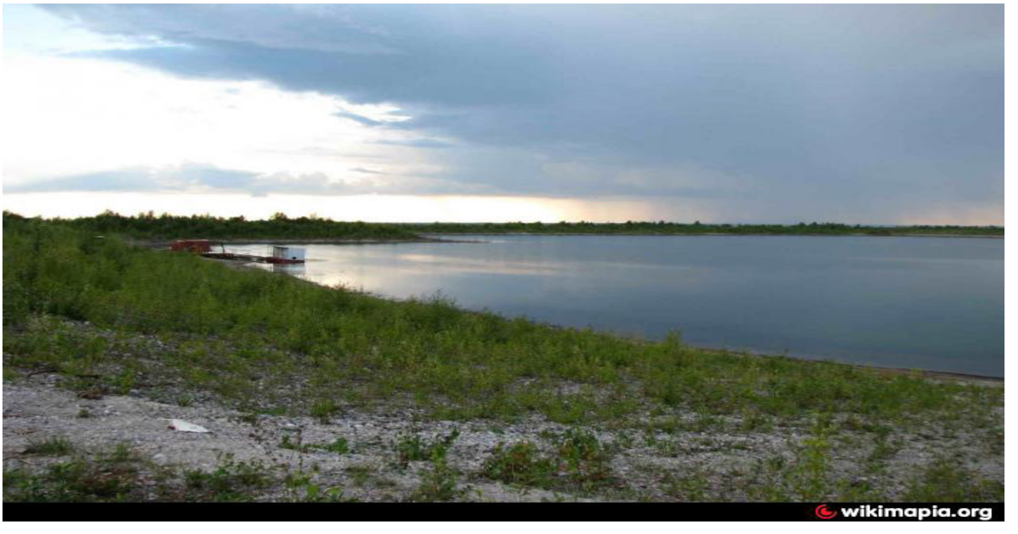

Figure.1. *Sludge storage unit БКПРУ-3*

enclosing dams of primary and secondary embankment, hydraulic dumps and other structural elements

Research results and their investigation

To substantiate the possibility of using the sludge storage facilities of potash production industry liquid wastes as a treatment plant for effluents clarification and sewage sanitation, the analysis of such facilities operating experience at the mining departments of PJSC Uralkali was carried out. By way of example, the operation of sludge storage unit BKPRU-3 is considered. Characteristics of the chemical composition of wastewater entering the sludge storage unit and of clarified (circulating) wastewater are shown in table. 1. As can be seen from the presented data, the content of suspended solids in the clarified waste water substantially reduces (purification efficiency is more than 99.9 %). In clarified circulating brines there is a decrease in the content of mineral impurities: the chloride ions content is reduced by 46 %, the dry residue content - by 45.6 %. The increase in ammonium ions share can be explained by the decomposition of organic amines used as flocculants.

Sedimentation rates for suspended solids with known granulometric composition in mineralized solutions at different temperatures were calculated (I. Studenov,2014). The sedimentation time for finely suspended impurities in mineralized waters depending on the temperature and the structure height is from 1.2 to 17.8 days. For effective deposition of fine impurities, the sludge storage unit capacity should provide at least 10 days' period for wastewater contact in the construction.

Complex chemical-physical and microbiological processes have place in sludge storage units; such processes provide effluents clarification, water mineralization degree changes by the depth, toxic organic substances degradation and water decontamination.

Main processes occurring in the sludge storage units:

1. *Waste water dilution by atmospheric precipitation.*

Analisys of the sludge storage units' operation at the PJSC Uralkali, water balance estimation for БКПРУ -1,2,3,4 sludge storage units demonstrated that the average dilution coefficient is in frames of 1,16 - 1,2.

2. *Water clarification due to the long-term ponding*

Durability of suspended matter ponding in the sedimentation pond (sludge storage unit) is > 10 days. It allows to achieve 99,9% removal of suspended solid particles (with particle size of <0,045 мм) from waste water.

Suspended fine clay particles sedimentation can be accelerated by their enriching coagulation in highly concentrated electrolytes solutions. Besides, particles coagulation in result of water freezing-defrosting is possible in winter and spring seasons.

3. *Processes of dissolution and crystallization for solid phase of clay-salt slurries*

The solid phase of clay-salt slurries includes sylvite KCl (mass content of KCl (expressed in solid content), % - 10,0 -12) and halite NaCl (mass content of NaCl (expressed in solid content), % - 18,0 - 20). The sludge is a coherent stable colloidal system, but in result of prolonged storage in the sludge storage unit the slow salts dissolution occurs. When the temperature regime changes under the influence of seasonal temperature fluctuations, salts solubility in water changes and their crystallization in the bottom part of the sludge storage pond is possible.

4. *Density stratification of mineralized water by the sludge storage pond depth*

In summer seasons the density stratification of mineralized water by the sludge storage pond depth is possible. In upper more heated water layers the solubility of salts, especially potassium chloride, increases, and, respectively, the density of the water layer, which then slowly sinks into the bottom horizons, increases too, i.e., density concentration convection of sodium-potassium chloride brines is observed. In the bottom layers the formation of saturated salt solutions is possible. At low temperatures, the density and viscosity of concentrated sodium and potassium chloride solutions (16-20 mass.%) increases, and the near-surface layers being heavier fall down, displacing the less dense layers. This phenomenon can also lead to temperature and concentration stratification through the depth of the sedimentary pond (sludge storage unit) and in winter seasons.

Estimation of freezing points for sodium and potassium chloride solutions demonstrated that at concentrations of sodium chloride of 15,0 – 18 % and potassium chloride of 9 - 12%, these values are (-11) - (- 15 °C) and (- 3,8) - (-5,9 °C) respectively. At low temperatures the solution viscosity increases, and formation of a layer representing suspension of ice and viscous solution has place. Depending on the capacity, the sludge storage ponds area can be 60-250 hectares, thus the unit structure parts at large distances from waste water input points can be covered with ice and snow. In periods of spring ice melting the layer of desalinated weakly-mineralized water will form. A.Sosnovsky in his paper (2011) demonstrates, that when melting about 50% of the artificial ice obtained by the salt water freezing, the concentration of sodium ions and chloride ions is 900 and 700 times lower, respectively, than that of the initial source water. According to R. Cherkasov (1989) and others, the boundary of the mineralization jump from 0 to 70,000 mg/L in chloride ion content is fixed at a depth of 5 m. During this period, it is possible to adjust the discharge of part of the clarified and desalinated waters into the water body, taking into account the hydrological and hydrochemical regimes of this water body. To determine the layer of desalinated water in the storage pond (sludge storage unit), it is proposed to carry out an interval sampling of clarified water with a depth step of 0.5 m, for example, at the distance of 100 m. The samples mineralization should be controlled by the content of chloride ion, potassium and sodium ions. Basing on the water samples analysis results, the depth of the mineralization jump is determined.

At this depth range (0-5 м) the average concentration of desalinated water ($C_{опр}$) is determined based on water samples chemical analysis results – Discharged water volumes should be calculated in such a way that the content of mineral impurities will not exceed the required normative indicators in the water body.

5. *Degradation of organic impurities under influence of halo-tolerant and halo-philic bacteria*

Waste water discharged into the sludge storage units includes organic impurities – ethoxylated amine, polyacrylimide, aliphatic amines, as well as mono- and polyaromatic compounds, which are persistent toxic substances (Bachurin & Odintsova, 2009). Reagents content is 3-5%. In recent years, studies have been conducted to identify halotolerant and halophilic bacteria and microorganisms in clay-salt slime and determine their ability to destroy toxic organic compounds. In the research performed by E. Korsakova (2013) it was found that there are actinobacteria of the *Actinomycetales type* (destructors of toxic organic compounds) in potash production wastes. *Rhodococcus wratislaviensis* KT112-7 strain, isolated from clay-salt slurries, is able to decompose toxic organic compounds, including ortho-phthalic and benzoic acid, in the presence of elevated concentrations of sodium chloride. The efficiency of destruction of toxic components is more than 80 %. *Rhodococcus whratislaviensis* KT112-7, extricated from clay-salt slurries, can destruct toxic organic compounds –*ortho*-phthalic and benzoic acids among them – in presence of sodium chloride with elevated concentrations. The toxic substance destruction effectiveness exceeds 80 %.

When necessary, for improvement of the efficiency of organic impurities removal from effluents it is advisable to add to effluents the *Rhodococcus whratislaviensis* KT112-7 microorganism strains produced from potash industry wastes.

6. *Waste water decontamination processes.*

In the sludge storage unit, water disinfection processes have place as a result of the influence of osmotic pressure caused by different salt concentrations in highly mineralized wastewater and in the cytoplasm of bacterial cells. High osmotic pressure leads to dehydration of microbial cells and their destruction. The effectiveness of pathogens destruction is 98-99%.

Therefore, sludge storage unit can be considered as a wastewater treatment complex – sedimentation pond which provides industrial effluents purification to the level corresponding to requirements for the circulating brine quality, and their return to the technological needs; and to carry out the regulated discharge of treated wastewater part into the water body.

For effective and environmentally safe operation of facilities the environment protection measures aimed at prevention of negative ecological effect of facilities should be provided at the design stage:

- construction of contour embankment around the perimeter of the pond area, preventing the spreading of brines beyond this area,
- to prevent brines filtration and their penetration into underground waters, along the bed of the sedimentation pond (sludge storage unit), as well as along the upper slope of contour embankment, it is necessary to install an anti-filtration screen made of geomembranes based on polymeric materials, for example, high-

pressure polyethylene-Corbofol HPDE 406, which provides tightness and soils and groundwater protection against contamination from sludge and brines.

- Arrangement of the drainage system under the filter screen for discharge of some volumes of groundwater, nipped through the sedimentation pond (sludge storage unit) bottom and brine sump and for draining of water sumped from the soil pores of the pond ground bed under the weight of wastewater entered for treatment;
- removal of surface water from the surrounding areas behind the protecting embankment of the sedimentation pond (sludge storage unit) by arrangement of interception ditches.

In order to reduce the degree of mixing of waste water and the clarified water flows and to reduce flows turbulence degree it is advisable to install the end output point at 1.5 to 2.0 m below the sedimentation pond surface. The wash-over point should be selected at a considerable distance from the location of the floating pump station.

In order to provide environmental safety in process of facilities operation the system of sewage treatment units control and environmental monitoring was developed.

Conclusions

Performed analysis of sludge storage facilities operation at Uralkali's mine departments, investigation of the processes occurring in the structures and mechanisms of water salinity reducing, calculation of the speed of fine clay particles sedimentation in mineralized solutions at different temperatures allowed to conclude that the sludge storage unit can be considered as a complex wastewater treatment plant – sedimentation pond.

The facility provides treatment of industrial wastewater to levels which meet the requirements to the circulating brines quality, as well as it gives the possibility of regulated discharge of treated water into the water body. Advanced arrangement of facilities, effective anti-filtration protection, use of modern instrumentation, continuous production and environmental monitoring of facilities will substantially reduce their environmental impact and ensure trouble-free operation of the system.

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