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THE STUDY OF PROPERTIES OF SODA PRODUCTION WASTES AS ANTI-ICING REAGENTS

Oleksandr Suvorin[1], Inna Kravchenko[1], Maryna Ozheredova[1], Yevhen Zubtsov[1], Václav Píštěk[2]

[1] Department of Chemical Engineering and Ecology, Volodymyr Dahl East Ukrainian National University, 59-a, Tsentralniy Ave., Severodonetsk, 93400, Ukraine
[2] Institute of Automotive Engineering, Brno University of Technology, 2896/2, Technická, Brno, 616-69, Czech Republic
kravchiv@snu.edu.ua

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Abstract. The article considers the possibility of reducing the man-made load on surface and ground waters in Lysychansk-Severodonetsk industrial agglomeration caused by numerous sludge collectors and tailings storage facilities of various industries formed many decades ago. The paper provides information on the location and technical condition of the sludge collectors of the liquidated "LYSSODA" manufacture (Luhansk oblast), the amount of waste currently stored in them as well as the impact of these wastes on the quality of groundwater in the area where the sludge collectors are located. The work shows one of several possible options for using such wastes as a valuable secondary mineral raw material for obtaining a marketable product. The averaged data on the chemical composition of the solid phase of sludge and indicators of the liquid phase composition are given. According to the results of the analysis of scientific and technical information, it has been found that such wastes can ultimately be used for the production of anti-icing reagents. The obtained results of research on the dependence of the freezing point of working solutions on the concentration of salts, including the added corrosion inhibitors (triethanolamine, hexamethylenetetramine), indicate the feasibility of using soda ash production waste to obtain effective liquid anti-icing reagents without a mechanical component, while the optimal amount of added corrosion inhibitors is 0.5 % wt. Such reagents can be used both undiluted at temperatures up to minus 20 °C and strengthened to 15–20 % wt. by calcium chloride at temperatures up to minus 40 °C with consumption on highways at the level of about 100 g/m^2 of the treated surface.

Keywords: soda production, wastes, composition, freezing point, anti-icing reagents.

1. Introduction

Throughout the world and in Ukraine in particular, the problem of disposal of production waste, both already accumulated and currently generated, has become urgent. A typical example of this is the sludge collectors of the former OJSC "Lysychanska Soda" located in Luhansk oblast within the boundaries of Severodonetsk Territorial Community. Since 1892, the plant had been producing soda ash with a capacity of 450,000 t/h and other chemicals using the Solvay method, but in 2011, it stopped operating and was liquidated. However, four sludge collectors are still filled. The total area occupied by the storage facilities is 177.6 hectares, and the total volume of waste stored there is about 20 million m^3 (~11.13 million tons). The main production waste pumped into the collectors was distillery liquid, brine purification sludge, wastewater with low salinity, and excess mother liquor.

The sludge collectors, the main features of which are given in Table 1, are located on the left bank of the Siverskyi Donets river (Fig. 1) in the water protection zone of the river within the floodplain surrounded by forests of the Emerald Network (Siverskyi Donets river valley in Luhansk oblast, UA0000315). They pose a serious threat to the

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region's environmental safety due to the worsening condition of the groundwater and pollution of the river basin of the main water artery. In addition, the collectors do not have protection or any fencing. Therefore, people spontaneously remove the waste from the body of the dams and the bowl of the collectors. Besides, due to unauthorized works and under the influence of erosion processes, the integrity and stability of the structures are damaged, which can lead to an uncontrolled emergency with environmental pollution.

Table 1

Main features of collectors (Nikolaieva et al., 2020)

№	Feature	Collector			
		No. 1	No. 2	No. 3	No. 4
1	Year of putting into operation	No data		1969	1976
2	Year of termination of operation	1960	1975	2011	2011
3	Object area, ha	No data	50	29	60
4	Water-surface area of collectors (estimated value), ha	33	56	27.6	44.4
5	Volume of removed waste, million tons	No data	3.5	1.079	4.127
6	Rated capacity of collectors, million m^3	No data		3.7	6

a

b

Fig. 1. Area maps: a – map-scheme of the sludge collectors of the liquidated OJSC "Lyssoda"; b – location of the sludge collectors relative to the Emerald Network

Near the water intake zones located in the immediate proximity of the sludge collectors, the Novosyrotyno water intake for industrial water supply was stopped completely in 2005, and the water intake from the remaining five water intake zones for drinking and household water supply decreased from 100.2 thousand m^3/day in 1993 to 20 thousand m^3/day in 2015 (Mokhonko, 2015). This reduction is a consequence of pollution due to filtration, primarily by chlorine (I), ammonium (I), and iron (II, III) compounds of groundwater of the alluvial aquifer up to 4878.9; 560.1 and 319.2 mg/dm^3 respectively as well as waters of the Upper Cretaceous aquifer up to 55454.54; 729.3 and 316.1 mg/dm^3 (LLC "Luhansk Geoecocenter", 2007), which exceeds the MAC of these compounds in fresh water by 14, 280 and 1064 times, while the total area of groundwater contamination has already exceeded 10.5 km^2 (Mokhonko et al., 2020). In addition, the collapse of bund walls of the sludge collectors taking place these days poses a threat of sludge getting directly into the Siverskyi Donets, leading to an environmental disaster (Nikolaieva et al., 2020). Therefore, the development and implementation of modern technology aimed at the disposal of this type of waste with the production of marketable products is an urgent task.

Sludge collector No. 1 has been recultivated, and liquid from sludge collectors No. 2 and 3 has completely evaporated, but there is still liquid in collector No. 4. According to our long-term observations (Zubtsov et al., 2020; Suvorin et al., 2020), the average compositions of sludge and liquid phases are presented in Tables 2 and 3, respectively.

Currently, the following areas of industrial processing of this type of waste have been developed with getting the following products: lump and chemically precipitated chalk; belite-based binder and building materials (blocks) based on them; additives into cement production (Suvorin et al., 2020; Mikhaylova et al., 2010; Tytarenko et al., 2020). However, given the composition of the solid and liquid phases, this sludge can be used as a raw material for the production of anti-icing reagents as well as additives to prevent the freezing of coal and ores during their transportation in winter.

Table 2

The average composition of sludge in sludge collector No. 4

Element	Ca^{2+}	Mg^{2+}	Fe^{3+}	Cl^-	SO_4^{2-}	Insoluble impurities	Moisture
Concentration, % wt.	32.0	1.2	0.23	0.48	1.34	2.2	11

Table 3

The composition and main indicators of the liquid phase in sludge collector No. 4

Indicator	Indicator value
1 Appearance	Colourless transparent liquid
2 Density, g/cm^3	1.13–1.14
3 Hydrogen pH indicator, units.	8.5–9.2
4 Content of mineral salts in the residue after roasting, %	23.2–24.5
5 Content of $(Ca+Mg)Cl_2$, % wt.	13.3–14.1
6 Content of NaCl, % wt.	6.1–6.4
7 Content of $SO4^{2-}$, % wt. (in terms of Na_2SO_4)	3.21–3.25
8 Content of CO_3^{2-}, % wt. (in terms of Na_2CO_3)	0.58–0.61
9 Content of NH_4^+, % wt.	0.051–0.052

Today, the market of products for removing ice from surfaces, e.g., for cleaning the road surface in winter, is represented by multi-component compositions that can contain both chemical and mechanical components. The function of the former is to melt ice and snow due to the formation of liquid mixtures with low melting (freezing) points. Mechanical components, mainly sand and diabase crumb are used to increase the adhesion of car wheels to the surface. There are three classes of anti-icing systems without a mechanical component (Optimum system, 2020; Zakrevskyi et al., 2016; "NIOCHIM", 2022):

a) salt-free, based on the use of solutions of organic substances with low melting points;

b) taking into account salts of organic acids;

c) based on chlorides of alkali and alkaline earth metals.

All these groups of reagents have their advantages and disadvantages. So, salt-free and organic acid salt-based anti-icing reagents are not highly effective at low temperatures even with a relatively high concentration of the target components in the aqueous solution (Simonova, 2004). They are relatively expensive since the raw material of waste salts of organic acids is small. The undoubted advantage of these reagents is their non-corrosiveness to most structural materials, including metals, and environmental friendliness, which means that they decompose quite easily in natural conditions and do not suppress the vital activities of urban and roadside fauna.

Mostly, inorganic salts are used as anti-icing reagents for city roads, primarily sodium, calcium, and magnesium chlorides in the form of dry salts or aqueous solutions. Among non-chloride reagents, a complex combination of magnesium nitrate and ammonium nitrate is recommended, i.e., a by-product of the production of mineral fertilizers, e.g., (Morozov et al., 2001) and magnesium nitrate (Orlova et al., 2001). The undoubted advantage of such reagents is low crystal hydrate points, short preparation time, and high solubility in water as well as low cost of chlorides, especially sodium and calcium. The negative feature of such reagents is their corrosiveness to metals. In addition, residual concentrations of chlorides of alkali and alkaline earth metals can negatively affect the environment (Borodina, Vyrozhemskyi, 2004; Siedov, Fomenko, 2019). However, taking into account the availability, the reagents based on chlorides of alkali and alkaline earth metals are still widely spread.

The purpose of the study is to assess the possibility of processing waste of the liquidated "LYSSODA" soda manufacture stored in large quantities in sludge collectors affecting the quality of surface and ground waters of the region and creating a threat of a landslide in the Siverskyi Donets river if the walls of the dam are destroyed.

2. Experimental part

Considering that soda ash production wastes contain SO_4^{2-}, CO_3^{2-}, NH_3^+ ions in addition to Ca^{2+} and Mg^{2+} chlorides, it is appropriate to determine the crystallization temperature of solutions depending on their composition and with the addition of corrosion inhibitors.

The clarified liquid phase of sludge with the averaged characteristics presented in Table 3 was used as the starting material. To strengthen solutions with $CaCl_2$ to a concentration of up to 15 and 20 % wt. there was used a crystalline product obtained by dissolving the solid part of the sludge in hydrochloric acid, filtering, evaporating, and drying at a temperature of 120 °C.

Triethanolamine ($(HO\text{-}CH_2CH_2)_3N$) according to TU 2423-168-00203335-2007 and hexamethylenetetramine (urotropin) $C_6H_{12}N_4$ according to TU 2478-037-00203803-2012 were used as corrosion inhibitors. According to the recommendations (Ukravtodor, 2021), inhibitors were added in the amount of 0.5 % of the mass of the starting solution.

The concentration of ions Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, CO_3^{2-}, NH_4^+ and total salinity were determined according to the known methods (Lure, 2012), and the freezing point was determined by the cryoscopic method (Kostrzhyckyi et al., 2008).

3. Results and Discussion

The results of the experiments (average values of 3 parallel experiments) are presented in Table 4. The freezing point (T_f) for sample 7 was calculated by the method (Stromberg, Semchenko, 2009) using the known data (Ravdel, Ponomareva, 1983).

Table 4

The freezing point of the studied solutions

№	The studied solution	T_f, °C
1	The starting solution diluted 4 times	-3.1 ±0.1
2	The starting solution diluted 4 times + $(HO\text{-}CH_2CH_2)_3N$, 0.5 % wt.	-3.9 ±0.1
3	The starting solution	-26.7±0.4
4	The starting solution + $C_6H_{12}N_4$, 0.5 % wt.	-27.4±0.5
5	The starting solution + $(HO\text{-}CH_2CH_2)_3N$, 0.5 % wt.	-27.7±0.6
6	The starting solution strengthened to a content of 15 % wt. by $CaCl_2$	-28.8±0.5
7	The starting solution strengthened to a content of 15 % wt. by $CaCl_2$ + $C_6H_{12}N_4$, 0.5% wt.	-30.6±1.1
8	The starting solution strengthened to a content of 20 % wt. by $CaCl_2$	-50.3±1.2
9	The starting solution strengthened to a content of 20 % wt. by $CaCl_2$ + $(HO\text{-}CH_2CH_2)_3N$, 0.5% wt.	-51.2±1.2

The given data show that with a total concentration of salts of 5.8–6.1 % wt. (samples 1 and 2), the freezing point of the solutions was from minus 3 to minus 3.2 °C. This practically corresponds to the reference freezing point of the $CaCl_2$ solution (minus 2.9 °C) calculated according to the method (Siedov, 2018).

The addition of triethanolamine to such solutions causes a decrease in the freezing point by 0.5–0.9 °C. For the starting undiluted but clarified solution from the sludge collector (sample 3), the experimentally determined freezing point is minus 26.7±0.4 °C, which is less than the reference value (according to the corresponding concentration of

$CaCl_2$) by 2.1 ÷ 2.3 °C and below the calculated value by ≈3.5 °C. This is more likely explained by the presence of sodium chlorides, sulfates, carbonates, and ammonia with a total content of 9.9 ÷10.3 % wt. in addition to calcium chloride, which contributes to lowering the freezing point in these solutions. The addition of corrosion inhibitors in the amount of 0.5 % of the solution mass to the starting solutions leads to a decrease in the freezing point by 0.2 ÷ 1.6 °C (Fig. 2).

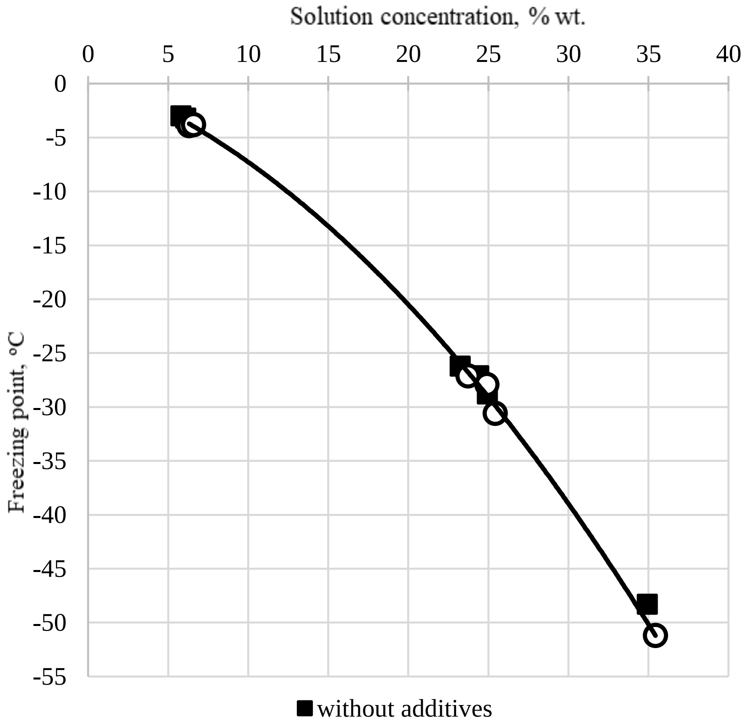

Fig. 2. Dependence of the freezing point of solutions on their concentrations

Strengthening of the starting solutions of $CaCl_2$ to 15 and 20 % wt. naturally leads to a decrease in the freezing point up to minus 28.8 °C and minus 50.3 °C, and the addition of corrosion inhibitors decreases it by another 0.6–0.8 °C. At the same time, for samples 7, 8, and 9, the freezing point was calculated by the equation of the approximate curve of the dependence of the freezing point on the total concentration of dissolved salts.

In accordance with the recommendations of the Uniform Rules for the Winter Road Maintenance PG.1-218-118:2005 regarding the norms for using anti-icing reagents, the tested undiluted solutions can be used at temperatures up to minus 20 °C at the consumption of 100 g/m^2.

4. Conclusions

Thus, the conducted research has shown that the liquid waste of the sludge collectors of soda production can be used as anti-icing reagents almost without additional processing. Using anti-corrosion additives of triethanolamine or hexamethylenetetramine in the amount of 0.5 % wt. does not lead to a noticeable decrease in the freezing point of solutions. Strengthening the studied liquid waste with $CaCl_2$ up to 15 and 20 % wt. helps use this solution at temperatures up to minus 40°C. The results of the conducted research also allow considering the liquid and solid wastes of soda manufacture as a valuable secondary mineral raw material, and their use for marketable products will allow reducing the man-made hazards to the surrounding natural environment in places where the waste is collected.

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