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THE DEVELOPMENT OF ENVIRONMENTALLY SAFE LITHIFICATION TECHNOLOGY FOR LIQUID SALT CONCENTRATES FROM THERMAL POWER PLANTS

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Keywords: heat power engineering, water treatment plants, liquid salt concentrates, moisture-absorbing sorbents, sodium polyacrylate.
Abstract. The paper presents the results of the development of environmentally safe lithification technology for liquid salt concentrates from water treatment facilities of thermal power plants. Sodium polyacrylate has been proposed as the basic moisture-absorbing component being a part of the polycomponent sorbent, used in the liquid salt concentrates lithification. Optimal mixtures of a multicomponent sorbent containing both sorbents and astringent mineral components have been developed. The optimal ratio of sodium polyacrylate and liquid salt concentrate is 1:40 (in weight parts). The toxicity determination of the produced samples by biotesting revealed the possibility of manufacturing safe solid product of 5th hazard class, which can be used as technical reclamation soil of the disturbed lands.

РАЗРАБОТКА ТЕХНОЛОГИИ ЭКОЛОГИЧЕСКИ БЕЗОПАСНОЙ ЛИТИФИКАЦИИ ЖИДКИХ СОЛЕВЫХ КОНЦЕНТРАТОВ ПРЕДПРИЯТИЙ ТЕПЛОЭНЕРГЕТИКИ

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Ключевые слова: теплоэнергетика, водоподготовительные установки, жидкие солевые концентраты, влагопоглощающие сорбенты, полиакрилат натрия.
Аннотация. В работе представлены результаты разработки технологии экологической безопасной литификации жидких солевых концентратов от водоподготовительных установок предприятий теплоэнергетики. В качестве основного влагопоглощающего компонента, входящего в состав поликомпонентного сорбента, используемого при литификации жидких солеконцентратов, предложен полиакрилат натрия. Разработаны оптимальные смеси поликомпонентного сорбента, содержащего как сорбенты, так и вяжущие минеральные компоненты. Установлено оптимальное соотношение полиакрилата натрия и жидкого солеконцентрата – 1:40 (в весовых частях). Определение токсичности полученных образцов методом биотестирования показало возможность получения безопасного твердого продукта 5 класса опасности, который можно использовать в качестве почвогрунта при технической рекультивации нарушенных земель.

Introduction

Heat generating plants are regular consumers of natural water in significant amount. The experts estimate the Russian share of electric power industry about 70% of the total fresh water consumption.

The power equipment reliability of the heat generation facilities is known to be directly related to the water quality for steam boilers and turbines of various operating pressure. Water quality is regulated by several regulatory documents, specifying the requirements for such indicators as total hardness, salinity, pH, dissolved oxygen, iron, copper, sodium, silicic acid, and other compounds [1-3].

To produce high-quality water at thermal power facilities, multi-stage water processing is used at water treatment plants (VPU) [4-6]. During the VPU operation, highly mineralized wastewater (liquid salt concentrates) amounts 10-30% of the total treated water consumption, which usually contains sludge consisting of calcium and magnesium carbonates, magnesium hydroxide, iron and aluminum, organic substances, sand, as well as various salts of sulfuric and hydrochloric acids with concentrations reaching tens of grams per cubic decimeter formed at various stages of the water treatment process [7]. The vital problem is represented by highly mineralized effluents containing sodium and calcium salts of chlorides and sulfates, which total concentration reaches 80,000 mg/dm^3 and many times exceeds the maximum permissible concentrations (MPC) for fishery water bodies. Such effluents cannot be directly discharged into the surface reservoirs [8-10]. Taking into account the existing MPC for contaminants in reservoirs, any highly mineralized effluents should be appropriately treated prior the discharge [11-13]. Thus, thermal power plants majority faces the problem of salt concentrate utilization. Options for its disposal are dilution and discharge into the surface waters, deep injection into wells, evaporation ponds. However, these technologies have limited application, as they are not economical, inefficient and environmentally unsafe. Bringing the wastewater mineralization to the MPC standards is possible applying, in particular, various evaporation equipment, but at the same time, significant operational and capital costs are required, which are sometimes comparable to the cost of overall water pretreatment to the required quality, therefore, the issue of creating drainless VPUs for thermal power plants is relevant.

The lithification technology is promising and comprises the transfer of liquid salt concentrate from VPU to the target product of 4-5th hazard class. It is based on the principle of pollutants immobilization, combined with the material production of the required physical and mechanical characteristics. The lithification application provides the local raw materials as well as natural sorbents use for its implementation. The lithification method principle consists in mixing salt concentrates with specially selected sorbents and mineral binding components (ash, cement), supplied in certain proportions. In the mineral environment, the processes of aluminosilicates and carbonates hydrolysis occurs, which are converted into a highly dispersed mineral matrix system with sorption capacity. The mineral matrix obtained in this way undergoes spontaneous regeneration, during which aluminosilicate binder compositions synthesis takes place. All kinds of organic and inorganic chemically active contaminants contained in waste are involved in their composition. Such approach using sorbents and mineral binders is known to be used for highly mineralized wastewater (filtrates) lithification at solid household waste landfills, where industrial waste - shale ash was used as a binder [14] for the liquid household and industrial waste lithification [15].

The research objective is to develop environmentally safe lithification of liquid salt concentrates of thermal power plants.

Research objects and methods

The Reverse Osmosis concentrate was studied in the research. Its composition is presented in Table 1.

The studied concentrate was 5.5 pH. The research was carried out using experimental plant for the liquid salt concentrates (highly mineralized wastewater) lithification formed after the water treatment unit, which schematic diagram is shown in Fig. 1.

Tab. 1. Reverse Osmosis concentrate composition

Component	Concentration, mg/l
Magnesium Chloride ($MgCl_2$)	116.4
Sodium Sulfate (Na_2SO_4)	2415.0
Sodium Bicarbonate ($NaHCO_3$)	3032.0
Sodium Carbonate (Na_2CO_3)	38.0
Calcium Chloride ($CaCl_2$)	168.6
Iron Chloride ($FeCl_3$)	6.0
Copper Sulfate ($CuSO_4$)	1.25
Total salinity	5777.25

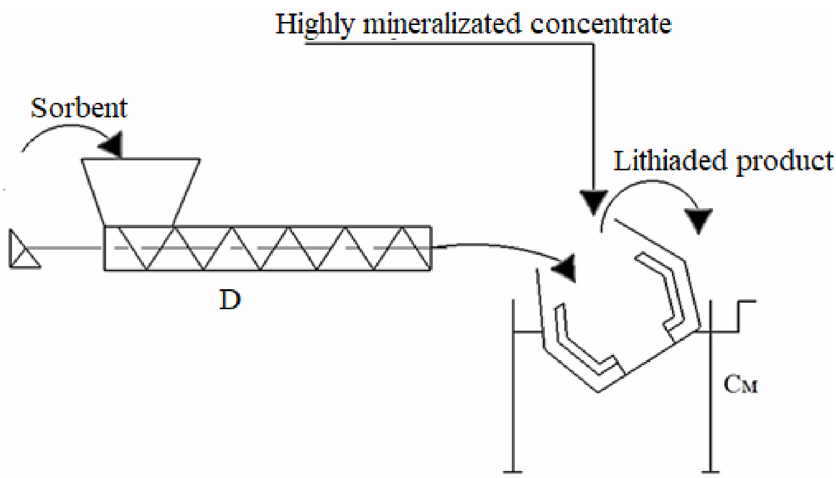

Fig. 1. Experimental plant for litification of liquid salt concentrate

The tested dry sorbents and mineral components of polycomponent moisture-absorbing sorbent are loaded into the dispenser D hopper and fed into the mixer with a screw dispenser, where liquid salt concentrate is added in the specified proportions. After 30 minutes mixing the resulting target product is discharged from the mixer.

Sodium polyacrylate was used in the research as the basic moisture-absorbing sorbent, being a part of the polycomponent sorbent. This polymer is able to absorb moisture exceeding its own weight in 10-50 times. Sodium polyacrylate is an anionic polyelectrolyte with negatively charged carboxyl groups in the main chain. The structural form of sodium polyacrylate is shown in Fig. 2.

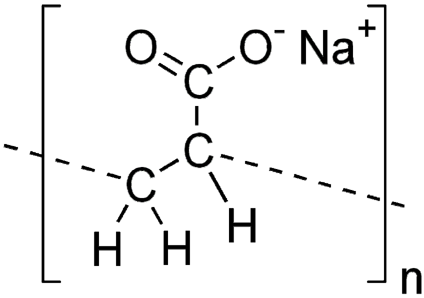

Fig. 2. The structural form of sodium polyacrylate

Sodium polyacrylate possesses good mechanical stability, high temperature resistance and strong hydration, providing the possibility to retain the liquid phase in the lithified material volume due to hydrogen bonds with water molecules.

In the experiments the sorbents and mineral binders were used, as shown in Table 2.

Tab. 2. Sorbents and mineral binders used in the development of a multicomponent moisture-absorbing sorbent

Item	Water extracts pH, units
Scrap red brick	8.41
Bentonite clay	9.84
Coal BAU-A	8.04
Quicklime (CaO)	11.95
Peat	5.84
Ash	10.,44
Cement	12.31
Sand	8.12
Scrap gas blocks (construction waste)	7.18
Sawdust	7.73

The toxicity of the target product samples was determined in compliance with methodological recommendations No. 01.019-07 "Determination of integral soil toxicity using the ECOLUME biotest on the Biotox-10M luminometer."

Conclusions dealing with the sample toxicity were made basing on the intensity changes of bacterial bioluminescence (imp/s) compared to the control for 30 minutes exposure. The decrease in bioluminescence intensity is proportional to the toxicity index T, determining the biotest response nature to environmental toxicity and is calculated by the following formula:

$$T = \frac{I_0 - I}{I_0} \cdot 100 .$$

where I_0 and I are the bioluminescence intensity of the control and the experiment respectively.

The method of determining the samples integral toxicity provides three threshold levels of toxicity:

– permissible level of toxicity at $T < 20$;

– the sample is toxic at $20 < T < 50$;

– high toxicity sample at $T > 50$.

In some cases, the toxicity index may be negative (at $I > I_0$), so it is concluded that sample is not toxic, and toxicity index takes zero value.

The aqueous extracts pH produced from the target product samples was determined using HANNA HI 83141 pH meter.

Results and discussion

The optimal ratio of concentrate salt to sodium polyacrylate comprised 1 wt. p of concentrate salt : 0.025 wt. p of sodium polyacrylate. At larger salt amount, the sorbent concentrate becomes insufficient, and at smaller amount of salt concentrate, the sorbent does not swell enough, has low contact surface and its application becomes irrational.

The compositions presented in Table 3 were prepared from the above-mentioned mineral components and sorbents.

Tab. 3. Compositions of the analyzed mixtures of their mineral components and sorbents

№	Mineral components and sorbents, wt.p.										pH, un.
	Scrap brick	Bentonite clay	Coal BAU-A	CaO	Peat	Ash	Cement	Sand	Scrap gas blocks	Sawdust	
1	-	20	20	-	-	-	-	20	-	-	5.5
2	-	-	-	-	5	10	-	10	-	-	10
3	-	-	-	10	-	10	-	-	-	15	11
4	-	10	-	-	5	-	-	-	-	5	5.5
5	-	10	10	-	-	-	-	10	-	-	5.5
6	-	-	5	-	-	-	10	-	-	5	9
7	-	5	-	-	-	5	5	-	-	-	9
8	-	-	10	10	-	10	-	-	-	-	11
9	-	-	-	-	-	-	10	10	-	10	9
10	-	-	-	10	5	-	-	-	-	10	11
11	-	-	-	-	5	-	5	10	-	-	8.5
12	5	10	-	-	5	-	-	-	-	-	5.5
13	5	-	-	-	-	10	-	-	-	10	8.5
14	10	-	10	-	-	-	-	15	-	-	5.5
15	-	-	-	10	-	-	-	-	5	15	11
16	-	-	-	-	5	-	-	10	5	-	5.5
17	-	10	-	-	-	-	5	-	5	-	10
18	10	-	-	10	-	15	-	-	-	-	12
19	5	-	-	-	5	-	-	-	10	-	8
20	-	-	-	-	-	-	-	10	5	10	7.5

The compositions prepared according to Table 3 from mineral components and sorbents mixtures at the experimental plant were alternately mixed with those supplied in the proportion with sodium polyacrylate and liquid salt concentrate to produce the target product. The experiments objective was to produce the target product with the crumbly, dense gel-like structure where the toxic components neutralization is achieved through the chemisorption absorption and further contaminants encapsulation in a mineral matrix.

Some of the produced samples turned out not to correspond to the task according to the matrix structure. Regarding the mixtures solidification (target product lack crumbly structure), the samples № 1, 7, 8, 14, 17, 18 did not participate in further experiments.

Besides Table 3 shows the water extracts pH from the target product samples, using a multicomponent moisture-absorbing sorbent. Most water extracts revealed their alkaline medium, basically depending on the quicklime or ash addition to these samples. These substances application in a multicomponent moisture-absorbing sorbent as mineral components causes significant increase on the target product alkalinity. Only two samples (Nos. 19 and 20) were characterized by close to neutral medium. Samples No. 4, 5, 12 and 16 were slightly acidic. At the next stage of the work, the toxicity of the obtained samples was determined. Due to the fact that biotesting should be carried out using aqueous extracts of samples having a neutral medium (pH 6-7), the pH of the mixtures was adjusted using a 10% solution of sulfuric acid and wood ash, based on the pH data of Table 3. The results of bioassay of the obtained samples of the target product are presented in Table 4.

Tab. 4. Results of the toxicity degree determining of the produced samples

№	Toxicity index T, un.	Error, %	Toxicity degree
2	-17.1	14.1	Non-toxic
3	-10.3	13.5	Non-toxic
4	76.7	11.9	High toxicity
5	-22	8.6	Non-toxic
6	46.3	8.9	Acceptable toxicity level
9	48.8	6.7	Acceptable toxicity level
10	48.5	11.8	Acceptable toxicity level
11	34.6	16.1	Acceptable toxicity level
12	63.8	19.8	High toxicity
13	94.8	3.5	High toxicity
15	51.8	2.7	High toxicity
16	-86.5	9.7	Non-toxic
19	-22.5	8.5	Non-toxic
20	85.5	1.8	High toxicity

According to the conducted bio testing results, the target product samples No. 2, 3, 5, 16 and 19 were considered non-toxic (toxicity degree – 0). Thus, these samples compositions can be attributed to 5 hazard class (practically non-hazardous waste) and recommended to be used as soils, since they contain peat, sand, clay, sawdust are soil components (according to GOST R 53381-2009 "Soils and grounds. The culture substrate soils. Technical conditions"), but lime and coal are used as additives. Construction inert finely crushed waste of red bricks and gas blocks can be additionally added as ripper. The soils obtained during the salt concentrates utilization can be used for the technical reclamation of disturbed lands as inert materials (spent quarries filler, cavities, recesses formed during open-pit mining, mining, sand, clay, crushed stone development, trench filling), etc.

Conclusion

The technology of environmentally safe lithification of liquid salt concentrates from water treatment facilities of thermal power plants has been developed, allowing to manufacture the target product that can be used as a soil for technical reclamation of disturbed lands, etc.

Sodium polyacrylate has been selected as the main moisture-absorbing sorbent, being a part of the recommended polycomponent sorbent. The optimal ratio of sodium polyacrylate and liquid salt concentrate is 1:40 (in weight parts). Mixtures of a multicomponent sorbent containing both sorbents and astringent mineral components have been proposed. Primarily mineral and organic waste, such as brick cutting, wood ash, sawdust have been suggested to be used as additional components. Bentonite clay, coal and calcium oxide can be used effectively.

Determination of the samples toxicity obtained by biotesting showed the possibility of producing a non-toxic solid target product of 5^{th} hazard class.

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НАЦИОНАЛЬНЫЕ ПРОЕКТЫ РОССИИ

НАУКА И УНИВЕРСИТЕТЫ

References

1. Van Winckel T., Cools J., Vlaeminck S.E., Joos P., Van Meenen E., Borregán-Ochando E., Van Den Steen K., Geerts R., Vandermoere F., Blust R. Towards harmonization of water quality management: A comparison of chemical drinking water and surface water quality standards around the globe // Journal of Environmental Management. 2021, vol. 298, p. 113447. DOI: 10.1016/j.jenvman.2021.113447

2. Uvarova A.S., Vitkalova I.A., Pikalov E.S. Application of ceramic waste for de-ironization of natural and wastewater by sorption // Ecology and industry of Russia. 2022, vol. 26, no. 3, pp. 34-39.
3. Chukhlanov V.Yu., Selivanov O.G., Pikalov E.S., Chesnokova S.M., Podolets A.A. Fluoride ions removal from water by lanthanum-containing ceramic material // Ecology and industry of Russia. 2018, no. 8, pp. 28-31.
4. Tarynina A.E., Goncharova L.K., Goncharov Yu.A. The current state of water treatment technologies at thermal power plants // International Scientific Journal Alternative Energy and Ecology. 2013, no.16(138), pp. 70-74.
5. Selivanov O.G., Pikalov E.S. Application effectiveness evaluation of sodium-cationite resins in the process of water softening for the heat generating plants operation // Water supply and sanitary engineering. 2022, no. 5, pp. 14-18.
6. Aliyeva O.O. Reverse osmosis in deep desalination schemes additional water for TPP // Deutsche internationale zeitschrift für zeitgenössische wissenschaft. 2021, no.19-1, pp. 47-51. DOI: 10.24412/2701-8369-2021-19-1-47-51.
7. Pervov A.G., Andrianov A.P., Gorbunova T.P., Yurchevsky E.B. Utilization technology of Reverse Osmosis concentrate in water treatment systems // Water supply and sanitary engineering. 2012, no. 8, pp. 20-26.
8. Filimonova A.A., Chichirov A.A., Chichirova N.D. The utilization of highly mineralized liquid waste from a chemical desalination water treatment plant of a TPP with the generation of electrical energy by reverse electrodialysis // Membranes and Membrane Technologies. 2021, vol. 3, no.5, pp. 344-350. DOI: 10.1134/S2218117221050059
9. Segev R., Hasson D., Semiat R., Improved high recovery brackish water desalination process based on fluidized bed air stripping // Desalination. 2012, vol. 281, pp. 75-59.
10. Pervov A.G., Efremov R.V., Spitsov D.V., Andrianov A.P., Gorbunova T.P. Membrane methods in drinking water supply: membranes selection, water quality forecast, concentrate utilization // Water supply and sanitary equipment. 2013, no.6, pp. 15-21.
11. Varaeva E.A. Purification of highly mineralized wastewater based on step liming // Scientific review. 2016, no.24, pp. 57-60.
12. Trifonova T.A., Povorov A.A., Shirkin L.A., Selivanov O.G., Ilyina M.E. Complex technology of solid waste landfills leachate processing // Ecology and industry of Russia. 2015, vol.19, no.11, pp.4-9.
13. Vlasova A.Yu. Resource-saving technologies of highly mineralized acid waste utilization from the ionite part of the combined water treatment plant at Sterlitamakskaya CHP // Izvestiya vyshchih uchebnykh uchebnykh zavody. Energy problems. 2022, no. 6, pp. 25-36.
14. Yazev A., Milutina N., Averyanova N., Velikoselskaya E., Politaeva N. Lithification of landfill filtrate as a method of its utilization // Ecology and industry of Russia. 2020, vol. 24(6), pp. 36-41.
15. Patent No. 2184095 RU. Mixture for neutralization and lithification of household and industrial waste, bottom sediments, sludge and oil-contaminated soils / V.M. Knatko, M.V. Knatko, E.V. Shcherbakova, A.V. Goncharov, N.V. Goncharova. – Appl. No 2001122534 from 07.08.2001; publ. 27.06.2002, Bul. No. 18.

Список литературы

1. Van Winckel T., Cools J., Vlaeminck S.E., Joos P., Van Meenen E., Borregán-Ochando E., Van Den Steen K., Geerts R., Vandermoere F., Blust R. Towards harmonization of water quality management: A comparison of chemical drinking water and surface water quality standards around the globe // Journal of Environmental Management. 2021, vol. 298, p. 113447. DOI: 10.1016/j.jenvman.2021.113447
2. Уварова А.С., Виткалова И.А., Пикалов Е.С. Применение керамических отходов для обезжелезивания природных и сточных вод методом сорбции // Экология и промышленность России. – 2022. – Т. 26, № 3. – С. 34-39.
3. Чухланов В.Ю., Селиванов О.Г., Пикалов Е.С., Чеснокова С.М., Подолец А.А. Очистка воды от фторид-ионов лантансодержащим керамическим материалом // Экология и промышленность России. – 2018. – №8. – С. 28-31.
4. Тарынина А.Э., Гончарова Л.К., Гончаров Ю.А. Современное состояние технологий водоподготовки на тепловых электростанциях // Международный научный журнал Альтернативная энергетика и экология. – 2013. – № 16 (138). – С. 70-74.
5. Селиванов О.Г., Пикалов Е.С. Оценка эффективности применения натрий-катионитовых смол в процессе умягчения воды для работы теплогенерирующих установок // Водоснабжение и санитарная техника. – 2022. – № 5. – С. 14-18.
6. Aliyeva O.O. Reverse osmosis in deep desalination schemes additional water for TPP // Deutsche internationale zeitschrift für zeitgenössische wissenschaft. 2021, no. 19-1, pp. 47-51. DOI: 10.24412/2701-8369-2021-19-1-47-51
7. Первов А.Г., Андрианов А.П., Горбунова Т.П., Юрчевский Е.Б. Технология утилизации концентрата установок обратного осмоса в системах водоподготовки // Водоснабжение и санитарная техника. – 2012. – № 8. – С. 20-26.
8. Filimonova A.A., Chichirov A.A., Chichirova N.D. The utilization of highly mineralized liquid waste from a chemical desalination water treatment plant of a TPP with the generation of electrical energy by reverse electrodialysis // Membranes and Membrane Technologies. 2021, vol. 3, no. 5, pp. 344-350. DOI: 10.1134/S2218117221050059
9. Segev R., Hasson D., Semiat R., Improved high recovery brackish water desalination process based on fluidized bed air stripping // Desalination. 2012, vol. 281, pp. 75-59.
10. Первов А.Г., Ефремов Р.В., Спицов Д.В., Андрианов А.П., Горбунова Т.П. Мембранные методы в питьевом водоснабжении: подбор мембран, прогноз качества воды, утилизация концентрата // Водоснабжение и санитарная техника. – 2013. – № 6. – С. 15-21.
11. Вараева Е.А. Очистка высокоминерализованных сточных вод на основе ступенчатого известкования // Научное обозрение. – 2016. – №24. – С. 57-60.
12. Трифонова Т.А., Поворов А.А., Ширкин Л.А., Селиванов О.Г., Ильина М.Е. Комплексная технология очистки фильтрационных вод полигонов твердых бытовых отходов // Экология и промышленность России. – 2015. – Т. 19, №11. – С. 4-9.
13. Власова А.Ю. Ресурсосберегающие технологии утилизации высокоминерализованных кислых отходов с ионитной части комбинированной водоподготовительной установки на Стерлитамакской ТЭЦ // Известия высших учебных заведений. Проблемы энергетики. – 2022. – № 6. – С. 25-36.

14. Язев А., Милютина Н., Аверьянова Н., Великосельская Е., Политаева Н. Литификация фильтрата полигонов ТКО как способ его утилизации // Экология и промышленность России. – 2020. – Т. 24(6). – С. 36-41.
15. Патент № 2184095 РФ. Смесь для обезвреживания и литификации бытовых и промышленных отходов, донных осадков, шламов и нефтезагрязненных грунтов / В.М. Кнатько, М.В. Кнатько, Е.В. Щербакова, А.В. Гончаров, Н.В. Гончарова. – Заявка №2001122534 от 07.08.2001; опубл. 27.06.2002, Бюл. № 18.

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