DOI https://doi.org/10.30525/978-9934-26-570-9-41

JUSTIFICATION OF ZERO LIQUID DISCHARGE TECHNOLOGIES FOR DESALINATION OF HIGHLY MINERALIZED WASTEWATER AT KRYVYI RIH IRON ORE BASIN (UKRAINE)

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INTRODUCTION

Freshwater scarcity is one of the most important global challenges of today, posing a serious threat to economic growth, water security, and ecosystem health worldwide.

Between 1900 and 1995, global freshwater consumption increased sixfold. Almost a third of the world's population lives in countries that consume water in volumes that exceed their actual reserves by 10%. At the end of the 20th century, the average water supply was 6,500 m^3 per capita. It is predicted that by 2050, with the world's population expected to reach 9 billion, water availability will be only 4,300 m^3 per year[1].

The presence of clean water is a necessary condition for the existence of all living organisms. Nevertheless, water resources are polluted by technogenic activities. Thus, a huge volume of freshwater has now become completely unsuitable for common use. First of all, this is due to the process of urbanization and industrialization. In the process of large industrial enterprises, wastewater is discharged into freshwater, which contains various pollutants. Many of them, getting into the human body, have a negative impact, leading to poisoning[2]. In addition, the population of cities is constantly increasing, which requires large expenditures to provide them with clean drinking water. According to expert calculations, 70% of fresh drinking water is used in agriculture, 60% of which is wasted due to improper use of irrigation systems. Today, there are a number of policy solutions aimed at reducing water losses, improving water management methods, and reducing the population's water needs[3].

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[1] United Nations Environment Programme (2024). Progress on Ambient Water Quality. Mid-term status of SDG Indicator 6.3.2 and acceleration needs, with a special focus on Health, Nairobi.

[2] Oleksandr Kovrov, Daria Kulikova and Artem Pavlychenko (2023). Statistical analysis of Samara River pollution impact on the population morbidity rate in Western Donbas (Ukraine). *IOP Conference Series: Earth and Environmental Science,* 1156 (2023) 012025. https://doi.org/10.1088/1755-1315/1156/1/012025.

[3] Bogardi, Janos & Gupta, Joyeeta & Nandalal, K D W & Salamé, Léna & Nooijen, Ronald & Kumar, Navneet & Tingsanchali, Tawatchai & Bhaduri, Anik & Kolechkina, Alla. (2021). Handbook of Water Resources Management: Discourses, Concepts and Examples. 10.1007/978-3-030-60147-8.

Wastewater recovery and reuse has become a growing trend over the past decade due to the increasing demand for clean water. Reusing wastewater reduces its volume and environmental risks and the pressure on the ecosystem due to the scarcity of freshwater. Reused wastewater is no longer considered harmful waste for the environment, but as an additional resource that can be used to achieve water sustainability.

This work aims to assess the current ecological state of surface water bodies of the Kryvyi Rih Iron Ore Region (Ukraine) and justify the reasonability of Zero Liquid Discharge (ZLD) technologies for desalination of mineralized wastewater.

1. Characteristics of the ecological state of surface water bodies of the Kryvyi Rih iron ore region

The Kryvyi Rih Iron Ore Basin (Kryvbas) is the largest basin in Ukraine with rich iron ore deposits, and the country's main mining center located in the Dnipro region.

Since the beginning of the industrial development of subsoil in Kryvbas, about 6 billion tons of iron ore have been extracted. Today, 18 deposits are simultaneously exploited in Kryvbas, which are developed by surface and underground mining.

The main objects of the mining and processing industry are concentrated on a relatively small area (330 km^2) within the Kryvyi Rih industrial and urban agglomeration or near its borders.

There are eight mines in the basin for underground mining of iron ore raw materials, which conduct mining operations in particularly dangerous underground conditions at depths of 800-1500 m. There are also two mines that have been restructured and operate exclusively in the hydroprotection mode.

Also, five large mining and processing plants (MPPs) with 10 quarries operate in the Kryvbas basin, with average depths of 250-450 m.

Over the past decade, operating mining enterprises in Kryvbas have annually pumped about 40 mln m^3 of groundwater from mines and quarries to the surface, including 21-22 mln m^3 of quarry waters and 16-17 mln m^3 of highly mineralized mine waters. These waters have a high content of chlorine, sulfate, sodium, potassium, magnesium, and calcium ions with increased levels of total mineralization from 5 g/l to 96 g/l with average mineralization up to 40 g/l[4].

The maximum capacities for using groundwater in the return cycles of mining enterprises in Kryvbas are limited to 28-30 mln m^3 per year. The

[4] Альтернативна схема (режим) акумуляції надлишків зворотних вод у ставку-накопичувачі в балці Свистунова та їх скидання в р. Інгулець. Розділ 1. Пояснювальна записка. // ПрАТ «УКРВОДПРОЕКТ». К. 2018. 58 с.

remaining 11-12 mln m^3 of excess return water is annually accumulated and temporarily held in a mine water storage pond.

The actual volumes of mine water pumped to the surface by enterprises of the Kryvyi Rih Iron Ore Basin from 2012 to 2017 are given in Table 1.

Under the current hydrogeological conditions in Kryvyi Rih, the cessation of the water discharges and flooding of any of the enterprises will cause a significant increase in the volume of groundwater inflow into the worked-out space and capital workings of neighboring mines. Under such conditions, mining and underground iron ore mining in the Kryvyi Rih iron ore basin will become impossible.

In the case of a mines shutdown, 1,105 mln t of rich iron ores and 4,614 mln t of unoxidized ferruginous quartzites will be flooded. As a result of the cessation of groundwater pumping in Kryvbas, the state will lose the opportunity to exploit one of the largest iron ore deposits in the world. The simultaneous flooding of all mines will lead to the development of the flooding process and changes in the physical and mechanical properties of rocks in the largest part of the area of central Kryvbas. In addition, the complete flooding of mines and quarries will lead to a rise in the groundwater level in most of the city territory and will cause flooding.

The increase in the groundwater level in the sedimentary layer will lead to a sharp intensification of exogenous processes and deformation in the upper layers of soils.

Table 1

Actual volumes of mine water pumped to the surface by enterprises of the Kryvyi Rih Iron Ore Basin[4]

Company name	**Actual volume of water pumped to the surface, thousand m3/year, by year:**				
	2013	**2014**	**2015**	2016	2017
“Ternivska” Mine	1584.4	1439.2	1368.4	1199.5	1389.8
“Kozatskaya” Mine	1232.2	1310.4	1136.6	929.3	1254.1
“Yubileyna” Mine	1002.4	1006.1	843.0	796.4	350.1
“Kolaczewski” Mine	159.3	146.1	126.0	136.0	136.9
“Pershotravneva” Mine	628.0	569.9	563.4	587.1	589.8
Total (Northern group of mines)	**4606.3**	**4471.7**	**4037.4**	**3648.3**	**3720.7**
“Pokrovskaya” Mine	1482.6	1466.5	1273.9	1287.8	1355.8
“Kryvorizka” Mine	3709.8	4416.6	4619.1	4784.3	4673.0
“Frunze” Mine	782.2	661.5	805.7	986.1	1390.7

Mining Department of PJSC “ArcelorMittal Kryvyi Rih”	3454.8	3229.0	3066.4	2791.1	2613.7
“Gigant-Hlyboka” mine	3326.5	3291.9	3121.8	2704.8	2556.8
Total (Southern group of mines)	**12755.9**	**13065.5**	**12886.9**	**12554.1**	**12590.0**
Total in Kryvbas Region	**17362.2**	**17537.2**	**16924.3**	**16202.4**	**16310.7**

The average annual chemical composition of mine waters pumped to the surface by Kryvbas enterprises is given in Table 2.

Mine waters (3-4 mln m^3/year) from the Northern group of mines are pumped into the tailings pond of PrJSC “Northern Mining and Processing Plant” (PrJSC “NMPP”), where they are used in the return water supply cycles of the plant. Periodically, due to the impossibility of using the entire volume of pumped out, both mine and quarry water in the technological cycles of ore enrichment at PrJSC “NMPP”, forced discharges of excess return waters from the tailings pond of the enterprise into the Inhulets River are carried out through its left tributary, the Saksagan River. After the discharge of excess return waters, the Saksagan River bed is washed by the water of the Southern Reservoir.

Table 2

Average annual chemical composition of mine waters pumped to the surface by enterprises of Kryvbas, by priority indicators[4]

Company name	**Chemical composition of mine water pumped to the surface, by priority indicators:**			
	dry residue, g/dm^3	**hardness, mmol/dm^3**	**Cl^-, g/dm^3**	**SO_4^{2-}, g/dm^3**
“Ternivska” Mine	11.15-24.63	23.7-75.2	5.26-13	1.38-1.97
“Kozatskaya” Mine	30.8-67.2	74.4-206	13.5-38.4	1.66-2.22
“Yubileyna” Mine	55.4-89.6	140.2-227	28.3-39.5	1.75-2
“Pershotavneva” Mine	2.4-4.8	20-35	0.68-1.55	0.56-1.5
“Pokrovskaya” Mine	57.7-62.5	68.03-77.3	35.81-36.16	1.62-1.64
“Kryvorizka” Mine	55-60	132.5	33.3	1.47
“Frunze” Mine	12.4-34.3	42.9-94.2	5.9-11.3	1.1-2.1
Mining Department of PJSC “ArcelorMittal Kryvyi Rih”	9.8-25.9	-	4.43-12.5	0.54-2.18
“Gigant-Hlyboka” mine	22.89-26.51	59.8-78.7	11.62-13.7	1.32-1.83

Mine waters (12-13 mln m^3/year) from the Southern group of mines are pumped into the mine water storage pond in the Svystunov basin.

The storage pond is designed for temporary accumulation of excess mine water during the growing season (from March 1 to October 31) with their subsequent discharge in the autumn-winter (inter-growing) period (from November 1 to February 28) in a volume of 10-12 mln m^3 into the Inhulets River, when there is no seasonal water intake for irrigation below the return water discharge point.

Due to certain hydrogeological features of the bed and the base of the protecting dam, the reservoir pond is an object of unfinished construction. For this reason, it is impossible to accumulate the entire annual volume of excess mine water (the temporarily permitted maximum volume of accumulation is 7.75 mln m^3, which corresponds to the water level in the pond of 86 m). Under such circumstances, the reservoir pond is filled annually to the recommended levels. If the reservoir pond is filled further, there may be a threat to the integrity of its bed and dam. In order to avoid an emergency and prevent a man-made disaster at the reservoir pond, the Cabinet of Ministers of Ukraine annually approves a special regulation for the discharge of mine water into the Inhulets River.

The average annual chemical composition of mine waters discharged into the storage pond and tailings storage facility of PrJSC "NMPP" by priority indicators is given in Table 3.

Table 3

Average annual chemical composition of mine waters discharged into the storage pond and tailings storage facility of PrJSC "NMPP", by priority indicators[4]

Years	Chemical composition of mine water (g/l) in					
	storage pond			tailings pond		
	Cl^-	SO_4^{2-}	mineralization	Cl^-	SO_4^{2-}	mineralization
2013	20.89	1.39	41.0	21,226	1,764	39,877
2014	20.75	1.37	38.0	25,341	1,729	47,126
2015	20,565	1,395	38.69	26,919	1,636	49,656
2016	20.2	1.37	38.0	22,501	1,673	41,516
2017	20.3	1.4	38.0	25,006	1,679	46,264
Average value	**20,282**	**1,358**	**38,863**	**22.99**	**1,733**	**43,143**

The concentration of salts in mine waters discharged from the storage pond varies within 38-41 g/l (on average about 39 g/l) and tends to increase (due to further deepening of mines, there is a need to pump out groundwater from deeper horizons, where the concentration of salts is higher, compared to upper horizons). Therefore, the discharge of excess mine waters leads to a temporary deterioration of the state of the water body below the discharge point. To reduce this negative impact and improve the qualitative state of the water body, the volume of mine water discharged into the Inhulets River is partially diluted (from 44 to 45 mln m^3) with water from the Karachuniv reservoir, located upstream of the discharge point. To fill this volume, Dnipro River water from the Kremenchuk Reservoir (about 60 mln m^3) is transported through the Dnipro-Inhulets Channel to flush the Inhulets River bed[5].

For the period from May to August (irrigation season), it is planned to continue releasing water from the Karachuniv Reservoir to ensure the regulatory quality of irrigation water at the water intake of the Inhulets irrigation system and to support recreation on the Inhulets River in the summer.

This regime of washing and rehabilitating the Inhulets River has been implemented annually since 2011. The approved system of transporting water from the Dnipro River and diluting excess mine water has shown an improvement in the ecological state of the water body, however, the current situation violates the regulatory framework and does not meet the goals and objectives of the EU Water Framework Directive[6]. In addition, due to a lack of funding, the Inhulets River bed has been washed by Dnipro River water in recent years by only 60% of the planned volume, which worsens the condition of the studied reservoir.

Surface and groundwater under the influence of the activities of enterprises of the mining and metallurgical complex of the industry have undergone constant negative changes in the regime of levels and quality. Intensive filtration of saline waters from the tailings pond and the accumulator leads to the formation of significant areas of groundwater contamination. Thus, the area with groundwaters contaminated due to filtration leaks from hydraulic structures of the mining and metallurgical complex is about 280 km^2. In turn, contaminated groundwater is an additional source of pollution of the surface runoff of the Inhulets and Saksagan rivers, which flow nearby.

Under such conditions, the surface waters of the Inhulets and Saksagan Rivers, within the Kryvyi Rih industrial district, have practically lost their natural indicators and properties due to the impact of technogenic activity. Firstly, their hydrological regime has changed due to 100% overregulation,

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[5] Індивідуальний регламент скидання надлишків зворотних вод гірничорудних підприємств Кривбасу зі ставка-накопичувача б. Свистунова у р. Інгулець у міжвегетаційний період 2024-2025. Проект. URL: https://www.spfu.gov.ua/userfiles/files/ri2.pdf (data of access: 02.03.2025).

[6] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a Framework for Community action in the field of water policy. URL: https://www.fao.org/faolex/results/details/en/c/LEX-FAOC023005/ (data of access: 20.02.2025).

and secondly, their mineral and microcomponent composition has undergone significant changes.

The results of water quality analysis at the hydropoint of the village of Andriyivka (below the point of discharge of return water from the reservoir pond) for the period from the beginning of September to the end of October (before the discharge of highly mineralized water during the inter-vegetation period) are given in Table 4.

Table 4

Water quality analysis at the hydropoint of the village of Andriyivka before the start of the discharge of highly mineralized mine waters[4]

Years	Concentrations, average over the observation period, mg/l		
	chlorides	sulfates	mineralization
2013	1216	797	3408
2014	1153	1241	3318
2015	1516	852	3748.5
2016	1086	975	3507
2017	1347	978	3557.5
Average value	**1204**	**939**	**3498**
Normative value	350.0	500.0	1000.0

All mentioned above causes a number of very serious negative consequences that affect not only Dnipro, but also Kherson and Mykolaiv regions, namely:

1. Periodic discharge of highly mineralized mine waters causes sharp changes in salinity in the Inhulets River.

2. In the villages adjacent to Inhulets in the Dnipro, Kherson, and Mykolaiv regions, there was an increase in the salinity of water in local water supply sources (significantly above the permissible standards of 1 g/l). Below the discharge point from the reservoir pond, the following exceedances of the maximum permissible concentration are recorded:

– in Mykolaiv region: chlorides by 3-10.3 times, sulfates by 7.4-8.7 times, total iron by 1.3-6 times, dry residue by 3.53-5 times;

– in the Kherson region: chlorides by 5.8-9.1 times, sulfates by 1.3-1.6 times, dry residue by 4.2-6.4 times, COD by 1.4-2.8 times.

3. Saline water enters the irrigation systems of Mykolaiv and Kherson regions, which are involved in irrigating tens of thousands of hectares of

fertile land. This has led and continues to lead to salinization of valuable agricultural soils.

The discharge of highly mineralized mine waters into the Inhulets River leads to huge economic losses in all three regions, resulting in crop losses, irreversible losses of thousands of hectares of saline lands, and the need for additional freshwater supply to villages and settlements.

An accurate assessment of annual economic and environmental losses has never been made, but according to expert estimates, it amounts to tens of billions of hryvnias annually. Therefore, the problem of disposing of highly mineralized mine waters in Kryvbas is an interregional problem, and including the huge economic effect, a state problem.

In the Inhulets River basin, the issue of bringing water use by mining enterprises in Kryvbass into compliance with the requirements of current legislation remains unresolved. In addition, the activities of mining enterprises pose a threat to Ukraine's failure to fulfill its international obligations to achieve “good” water status.

Several solutions have been proposed to resolve this problem:

– development of an alternative mine water management scheme;

– increasing the volume of Dnipro River water supply for washing the channel and ecological improvement of the Inhulets River;

– implementation of effective technologies to reduce the level of natural and man-made pollution of highly mineralized mine and quarry waters before their discharge into water bodies.

2. Ways to solve problems related to improving the ecological state of surface water bodies of the Kryvyi Rih Iron Ore Region

In recent years, the problem of wastewater has become increasingly acute and relevant all over the world, including in Ukraine. In the process of economic activity, modern society consumes a large amount of water, most of which becomes contaminated with various substances. Their release into the environment causes significant harm, so they are subject to mandatory treatment. To ensure a highly effective treatment process, it is necessary to use special equipment and technological complexes which allow achieve the established environmental standards for wastewater treatment. Such equipment allows decrease the wastewater pollution to acceptable environmental standards.

Zero Liquid Discharge (ZLD) technologies represent an important direction in environmental safety and water treatment. These new technologies completely eliminate the discharge of contaminated wastewater into surface water bodies, which allows industrial enterprises to meet strict environmental discharge standards and achieve the highest degree of water recovery (90-98% of treated industrial water is suitable for reuse, for example, irrigation), as well as purify and recover valuable components from wastewater streams, such as sodium sulfate and chloride, potassium sulfate, caustic soda, gypsum, lithium, etc.

It should be noted that ZLD technologies are beneficial for managing highly mineralized streams, as they allow water reuse, reduce environmental impact and pollution risks, and extract valuable components in the form of residual solids (salts) before their disposal for additional revenue.

Typically, the ZLD process includes three main stages (Fig. 1):

1. ***Pretreatment*** (physicochemical and/or biological) – used to reduce the amount of insoluble impurities, turbidity, and organic matter content to ensure reliable operation of subsequent equipment used in the process flow.

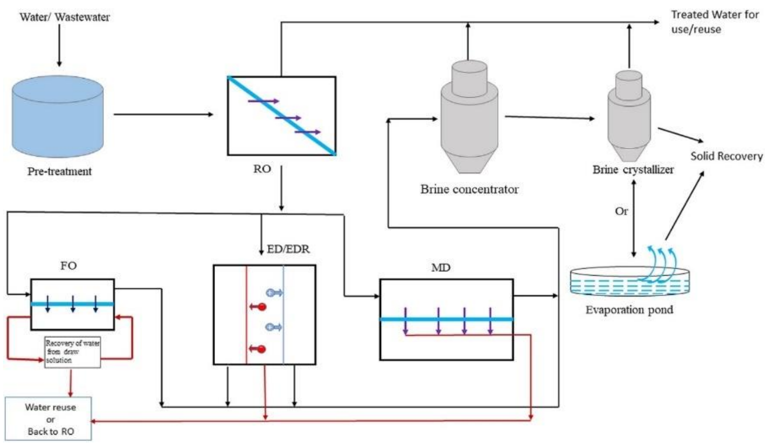

Fig. 1. Typical scheme for industrial wastewater treatment using ZLD technology

(Source: https://images.app.goo.gl/4VAXM7f5MUfJD3rYA)

2. ***Concentration of dissolved substances***. Over the past few decades, membrane desalination technologies for saline water (reverse osmosis RO, electrodialysis ED, or a combination of RO+ED) have been increasingly developed. Among them, the desalination of saline water by reverse osmosis is considered one of the most promising technologies for the sustainable provision of freshwater resources.

The RO process for treating saline water is particularly attractive due to the high selectivity of the membranes, which allow the solvent (freshwater) to pass through while the solute molecules and ions do not.

The most important advantage of the RO method is its low energy consumption. The specific energy consumption of the saltwater desalination process has been reduced from 20 kWh/m^3 (1980) to less than 3-4 kWh/m^3 by the development of highly efficient devices (high-pressure pumps, high-performance RO membranes, etc.). These technologies concentrate the feed water stream to high salinity and are capable of recovering up to 40-55% of the distillate at a pressure of 55-70 bar when desalinizing salt water (seawater)[7].

Recently installed large SWRO plants can produce freshwater at a cost of less than 0.5 USD/m^3, which is significantly lower than the cost of thermal desalination and much lower than the cost of SWRO plants built 30 years ago (desalination cost was higher than 2 USD/m^3)[7]. After pretreatment, the saline water is fed into the RO system to produce distillate (Fig. 2).

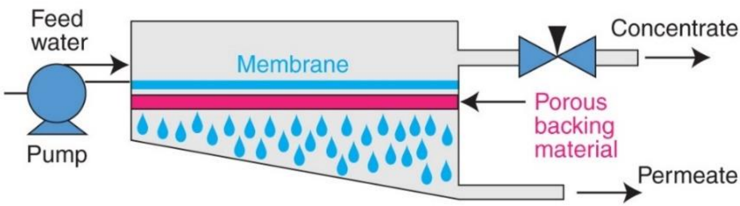

Fig. 2. Basic diagram of the reverse osmosis process

(Source: https://images.app.goo.gl/EdWfb36M27qNMREK6)

By removing contaminants and reducing salt concentration, water treated by reverse osmosis can meet the necessary standards for reuse.

Thus, reverse osmosis allows separation, concentration and recovery of valuable chemicals present in wastewater. This can lead to significant cost savings and reduce the industry's environmental impact.

3. ***Thermal treatment.*** An evaporation system allows efficient and affordable conversion of a portion of the water-based waste into steam, leaving contaminants with higher boiling point. This can eliminate the need for wastewater discharge and/or significantly minimize the amount of waste that needs to be transported off-site.

Evaporation is a clean process that does not add contaminants to those already present in the liquids to be treated. The equipment takes up little space, is relatively easy to maintain and has a long service life. In addition, the resulting condensate is of high quality, allowing it to be reused.

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[7] Seawater Reverse Osmosis (SWRO) Desalination: Energy consumption in plants, advanced low-energy technologies, and future developments for improving energy efficiency. Edited by Seungkwan Hong, Kiho Park, Jungbin Kim, Abayomi Babatunde Alayande and Youngjin Kim. IWA Publishing. DOI: https://doi.org/10.2166/9781789061215. ISBN electronic: 9781789061215. Publication date: May 2023.

At a certain evaporation pressure, the boiling point of the solution increases with the increase in salt concentration. At the same time, the higher boiling point leads to higher electricity consumption to maintain the heat transfer temperature difference. Therefore, the electricity consumption is highest at the saturation concentration.

That is why the processing of reverse osmosis concentrate is usually based on a combination of evaporation + crystallization technologies. In this process, the boiling, evaporation and crystallization occur at the saturation concentration. Therefore, the system consumes more compression power. One possible method of reducing the compression power is to first pre-evaporate part of the water at a lower concentration and then evaporate and crystallize the solute at the saturation concentration.

The proposed double-effect system (evaporation + crystallization) can save more energy than the single-effect system (evaporation).

Currently, thermal and mechanical evaporation methods are used for water desalination. High operating and energy costs are the main limitations of the industrial application of thermal evaporation technologies. Mechanical vapor recompression (MVR) is an advanced energy-saving technology for separating large volumes of wastewater with high flow rates and low energy consumption (Fig. 3).

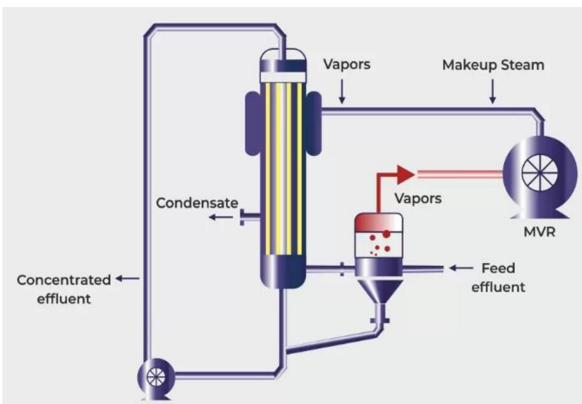

Fig. 3. Scheme of evaporation of concentrated wastewater solution using MVR technology with forced circulation (FC)

(Source: https://images.app.goo.gl/9Twu)

MVR technology allows the vapor generated by the evaporation of a solution to be compressed to a higher pressure and temperature using only electrical energy and reused as an energy source. The ability of MVR technology to recover heat for reuse means that it will play a key role in decarbonizing process heat[8].

The secondary steam produced in the evaporator is compressed by a compressor, which increases its temperature and pressure. As the pressure increases, the saturation temperature also increases. This increase in temperature leads to a temperature difference between the exhaust steam and the working fluid. The temperature difference transfers heat through a heat exchanger to boil the wastewater entering the treatment. Since the system operates in a closed loop, where the steam is recompressed rather than released into the atmosphere, the evaporator design increases environmental friendliness and minimizes heat loss.

The main advantage of the MVR evaporation system is that the evaporators are known for their high energy efficiency. Unlike alternative thermal vapor recompression (TVR), mechanical vapor recompression does not require additional fresh steam supply. Since no liquids are mixed, all existing steam can be compressed for energy recovery. In this case, the total energy consumption is reduced by 90% or more (rotary compressor and recirculation pumps consume 30-50 kWh/t of distillate). The reduction in energy consumption translates into economic benefits for industrial processes. Due to their energy efficiency, MVR evaporator designs can lead to lower operating costs in the long term. That is why MVR evaporators are becoming increasingly popular as energy prices rise.

Other advantages of MVR technology include:

– reduction of wastewater output by 97%, which allows obtaining high-quality water with its reuse for consumer needs;

– generation of a minimum amount of solid waste (sludge, concentrate) with the possibility of their further reuse with an additional profit or spending minimal funds on their disposal;

– low boiling points – 80-90°C;

– compared to traditional evaporators, the temperature difference is minimal, which guarantees gentle evaporation and increased quality of the finished product;

– compact evaporator design, occupying only 50% of the area of a traditional evaporator;

– no cooling water is required for steam condensation;

– all equipment provides automatic operation and can operate stably for a long time, requiring minimal control;

– ease of use.

[8] Liu, L. & Zhang, J.-J & Liu, Y. & Zhang, S.-F. (2014). Application of mechanical vapor recompression technology in evaporation. Huaxue Gongcheng/Chemical Engineering (China). 42. 1-5. 10.3969/j.issn.1005-9954.2014.11.001.

Crystallization plays a key role in ZLD systems, in which liquid effluents are subjected to a series of processes to produce dry waste and a stream of clean water by cooling, evaporation or chemical reaction[9].

The operation of a crystallizer is very similar to that of a vacuum evaporator, except that it is designed to evaporate all the solvent and obtain a crystalline product (salts NaCl, Na2SO4, etc.).

This technology can produce a solid concentrate with its subsequent use as by-products or raw materials (salts, acids, minerals, metals, oils, fertilizers, etc.), which in many cases can be recycled.

The main advantages of the crystallization plant include:

– minimization of the amount of waste that needs to be managed;

– significant reduction in waste management costs, including transportation and management;

– reduction of greenhouse gas emissions during waste transportation.

Vacuum crystallizer or evaporative cooling crystallizer is a modern equipment for the final treatment of saline wastewater (crystallization) in various industries. Due to its simple structure, it has low cost and high production capacity.

Vacuum evaporation crystallizers with mechanical vapor recompression (MVR) and forced circulation (FC) (Fig. 4), operating on electrical energy, are the most suitable for the treatment of wastewater concentrates with a high degree of mineralization, for example, the recovery of sodium chloride, sodium sulfate, ammonium chloride, ammonium sulfate, etc[10].

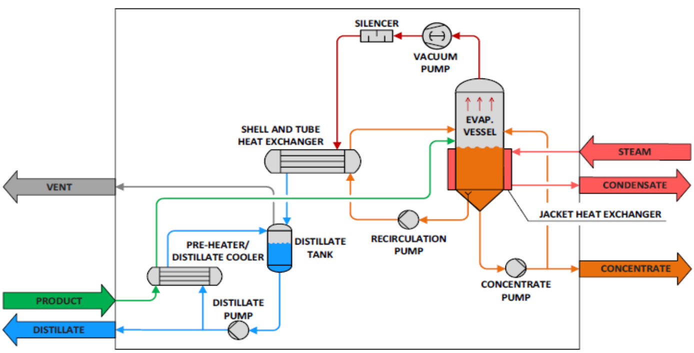

Fig. 4. Typical crystallization scheme using MVR technology with forced circulation (FC)

(Source: https://condorchem.com/en/evaporators/desalt-mvr-fc-1500-2500/)

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[9] Desarnaud, Julie & Noushine, Shahidzadeh. (2011). Salt crystal purification by deliquescence/crystallization cycling. EPL (Europhysics Letters). 95. 48002. 10.1209/0295-5075/95/48002.

[10] DESALT MVR FC crystallizer. URL: https://condorchem.com/en/evaporators/desalt-mvr-fc-1500-2500/ (data of access: 27.02.2025).

The crystallizer is a cylindrical vertical evaporation vessel with a conical bottom to facilitate the separation of solids. The evaporation vessel contains a heat exchanger with an external jacket to provide a small amount of steam during the heating phase and during operation to maintain the temperature. In addition, the vessel is equipped with an external shell-and-tube heat exchanger. Due to the recirculation pump, the process fluid flows inside the tube bundle at high speed, obtaining the energy necessary for crystallization. This avoids stratification on the exchange surface.

A vacuum pump (Roots blower) draws water vapor from the evaporation tank, compresses it to atmospheric pressure, and pumps the compressed vapor into the evaporator's condensation zone (shell and tube heat exchanger). This vapor is used as a heat source to re-evaporate the wastewater concentrate coming from the evaporator.

Condensation of the evaporated brine occurs in a shell-and-tube heat exchanger through which the concentrate to be processed passes.

The condensate is stored in a distillate tank and removed using a distillation pump.

The preheater transfers heat to the incoming wastewater distillate.

The crystallizer uses saturated steam for start-up and during operation.

The entire crystallization process is fully automated.

Thus, the implementation of the proposed ZLD technology for desalination of highly mineralized mine waters will promote sustainable water use, reduce the pressure on natural water resources, and increase the efficiency of production processes. This could be an important step in solving water shortage and environmental challenges.

All the equipment included in the proposed ZLD technology is powered by electricity. This makes it possible to use renewable energy sources, such as solar energy, to drive the main desalination processes instead of fossil fuel energy. As technologies continue to improve, freshwater becomes scarce, fossil fuel prices increase, desalination using renewable energy sources becomes more economically viable.

Despite the significant advantages of using solar energy, solar power plants also have disadvantages, one of which is the removal of large areas for the installation of solar modules. To work effectively, solar panels must occupy a fairly large area, which can be a problem in urban environments or on small land plots (the greater the power of the solar power plant, the more space is required for it).

To solve this problem, it is proposed to install a floating solar installation, which is a set of solar panels that must be attached to a structure that holds them above the water surface, on an artificial reservoir of the Kryvyi Rih Iron Ore Basin – a mine water storage pond located in the Svystunov Bay (Fig. 5).

Floating solar power plants (SPP) are an innovative solution in the field of renewable energy, which is an array of photovoltaic modules installed on special platforms (pontoon structures) placed on the water surface. Places for installing floating SPP can be former coal or sand quarries, other technical reservoirs (dams, canals, reservoirs, etc.), where swimming is usually prohibited for safety reasons.

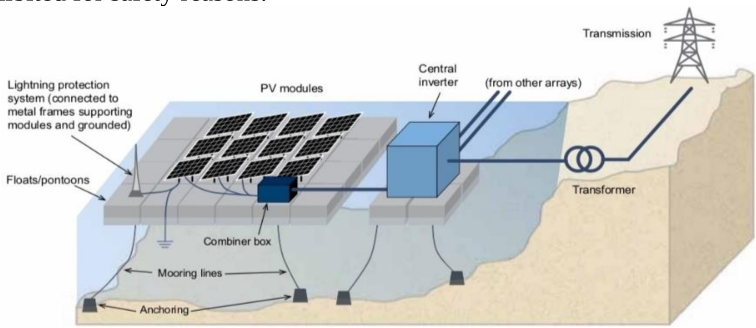

Fig. 5. Schematic representation of a typical large-scale FPV system

(Source: https://images.app.goo.gl/2naBt4aGTpU8abDM6)

Installing solar panels on a water surface has a number of advantages:

1. Solving the problem of land shortage. To install a powerful SPP, it is necessary to allocate a fairly large plot of land that could potentially be used for other purposes. Its long-term lease, especially near large cities, requires significant costs, which leads to an increase in the cost of solar electricity.

For agricultural lands, the legislation prohibits changing their status, and, as a result, makes it impossible to install SPP on them.

Additionally, installing solar panels on the water's surface reduces the need for tree removal, which is common with some larger solar projects.

2. Water is a surface with excellent reflectivity. Installing double-sided solar panels allows you to absorb reflected solar energy, which significantly increases the amount of electricity generated compared to installing similar solar panels on land.

3. Water is a natural radiator. Solar panels are durable and can operate at quite high temperatures. However, as with other electronics, power output decreases at higher temperatures. The efficiency of a solar panel decreases as the temperature increases. The surface of the water on which floating solar panels are placed helps to cool the equipment. This helps to avoid losses in electricity generation caused by heating of the panel surface (the efficiency of solar panels increases by 10-15% compared to ground-based installations). In addition, it extends their service life.

4. Additional environmental effect. Using renewable energy technologies helps reduce emissions of greenhouse gases and other pollutants into the atmosphere, which will positively impact the environment and human health.

Floating SPP can improve the condition of a reservoir, contributing to the preservation of biological diversity. The lack of sunlight prevents the development of some types of algae, thereby keeping the water cleaner and can become a natural habitat for various types of aquatic organisms.

By covering the water surface, solar panels reduce the amount of water evaporation, which is very important for regions with low water levels.

For the latitudes of Ukraine, monocrystalline solar panels are more advantageous. Due to the higher quality material (pure silicon), they have better performance at low light levels (in cloudy conditions). This is very important for electricity generation in the autumn-winter period, especially when using solar panels in Ukraine. In addition, monocrystalline elements work more efficiently in frosty weather, so using such solar panels in the winter is more practical.

The efficiency of monocrystalline panels can reach 20-25%. These panels will produce more electricity than other elements. Such high performance allows you to use a smaller area allocated for placing batteries. In addition, they have a long service life – at least 25 years.

3. Justification of the parameters for implementing the proposed ZLD technology for processing highly mineralized mine waters using the example of the Southern group of mines of the Kryvyi Rih iron ore basin

The justification of the parameters for the implementation of the proposed ZLD technology was carried out for the Southern group of mines of the Kryvyi Rih iron ore basin, which discharge their highly mineralized wastewater into a storage pond located in the Svystunov basin. The volume of water pumped to the surface, which requires desalination, is assumed to be $Q_{feed} = 13{,}000$ mln m^3/year with a total mineralization $C_{feed} = 39$ g/dm^3 (average values in Tables 1 and 3).

One of the conditions for the effective and long-term operation of reverse osmosis plants is the need to introduce a preliminary preparation stage into the general technological scheme for processing highly mineralized wastewater, which consists in the sequential conduct of reagent softening and clarification of mine water entering the desalination process. Proposed in the work[11] the pre-treatment of mine water reduces the load on the reverse osmosis unit and ensures optimal membrane module operation.

[11] Kovrov, O., Pavlychenko, A., & Kulikova, D. (2024). Development of the wastewater treatment technology for the mine ‘Ternivska’ of the Kryvyi Rih iron ore plant. *Environmental Technology*, 1-14. https://doi.org/10.1080/09593330.2024.2371080.

Next, the pre-treated mine water is fed by a high-pressure pump to a reverse osmosis unit, which is designed to desalinate liquid with a mineralization of 25 to 45 g/dm^3.

The selectivity of membrane modules for desalination of saline water is 99.3-99.7%. The working pressure is 50-90 bar (5-9 MPa), the working temperature is up to 35°C, the working pH range is 1-12. The degree of recovery of a reverse osmosis plant for saline water is on average 40-50%, based on the fact that the degree of recovery of one membrane element should be 10-12%[12].

Polyamide hollow fiber membranes are usually used for desalination of saline water, reinforced with fiberglass to increase their strength. Such membranes meet the more modern requirements of industrial water treatment and are able to purify saline water without losing productivity and without wearing out over a long service life (up to 2-4 years).

If we assume the degree of recovery of the reverse osmosis installation of saline water R=45% (average value), then with the total amount of mine water supplied for desalination Q_{feed}=13000 mln m^3/year (1484.02 m^3/hr), the amount of distillate obtained will be:

$$Q_{distillate} = Q_{feed} \cdot 0.45 = 1484.02 \cdot 0.45 = 667.81 \text{ m}^3\text{/hr.}$$

In this case, the amount of reverse osmosis concentrate obtained will be:

$$Q_{concentrate} = Q_{feed} - Q_{distillate} = 1484.02 - 667.81 = 816.21 \text{ m}^3\text{/hr.}$$

If we assume the degree of selectivity of membrane modules S=99.5% (average value), then with a total mineralization of mine water C_{feed}=39 g/dm^3, the concentration of salts in the distillate obtained after the reverse osmosis installation will be:

$$C_{distillate} = C_{feed} \cdot (1 - S) = 39 \cdot (1 - 0.995) = 0.195 \text{ g/dm}^3.$$

In this case, the salt content in the resulting reverse osmosis concentrate will be:

$$C_{concentrate} = \frac{1}{(1-R)} \cdot C_{feed} = \frac{1}{(1-0.45)} \cdot 39 = 70.91 \text{ g/dm}^3.$$

Thus, in a reverse osmosis plant, almost half of the pre-treated mine water is filtered through membranes to produce freshwater with a salt content of approximately 200 mg/dm^3. The remaining water flows out of the modules as a concentrate with a total salt content of approximately 71 g/dm^3.

A solution of this concentration is further processed by evaporation, since with its further concentration by reverse osmosis there is a risk of intensive deposition of hardness salts on the membranes.

[12] Membrane specifications Hydranautics SWC SWC6-MAX. URL: https://surl.li/rrklek (data of access: 14.03.2025).

For the evaporation of reverse osmosis concentrate, it is proposed to use an evaporator with MVR and forced circulation[13]. Forced circulation ensures a constant and efficient heat transfer from the heating element to the liquid. This results in faster evaporation and increased thermal efficiency. This results in faster evaporation and increased thermal efficiency. Such evaporators can be easily scaled up or down to handle different flow rates and liquid volumes, making them suitable for both small and large-scale applications. The high liquid velocity and turbulent flow in the system minimize the risk of scale formation and fouling on the heat transfer surfaces, increasing the evaporator's overall efficiency and service life. Forced circulation evaporators effectively concentrate wastewater, recovering valuable resources and reducing sludge volume for disposal. They play a key role in desalination plants, producing freshwater from seawater or brackish water.

The distillate production capacity can reach 200 m^3/hr. The evaporation temperature is 50-90°C. The evaporator recovers up to 95-99% of freshwater for reuse.

If we assume the degree of recovery in the freshwater evaporator R=97% (average value), then with a total amount of reverse osmosis concentrate Q_{feed}=816.21 m^3/hr, the amount of distillate obtained will be:

$$Q_{distillate} = Q_{feed} \cdot 0.97 = 816.21 \cdot 0.97 = 791.724 \text{ m}^3\text{/hr.}$$

In this case, the amount of concentrate obtained from the evaporator will be:

$$Q_{concentrate} = Q_{feed} - Q_{distillate} = 816.21 - 791.724 = 24.486 \text{ m}^3\text{/hr.}$$

The salt content of the resulting distillate is 30-100 mg/dm^3. The salt content in the resulting evaporator concentrate will be:

$$C_{concentrate} = \frac{1}{(1-R)} \cdot C_{feed} = \frac{1}{(1-0.97)} \cdot 70.91 = 2363.67 \text{ g/dm}^3.$$

The solid product obtained after evaporation is a mixture of mineral salts (sodium chloride) with a moisture content of 8-10%. For its crystallization, it is proposed to use a vacuum evaporation crystallizer using mechanical vapor recompression (MVR) and forced circulation (FC)[10].

The crystallizer can produce up to 2 m^3/hr of distillate. The evaporation temperature is 90°C.

If we assume the moisture content in the solid product W=10% (maximum value), then with a total amount of evaporator concentrate Q_{feed}=24.486 m^3/hr, the amount of distillate obtained will be:

$$Q_{distillate} = Q_{feed} \cdot 0.1 = 24.486 \cdot 0.1 = 2.449 \text{ m}^3\text{/hr.}$$

In this case, the amount of solid product obtained (NaCl) will be:

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[13] ENVIDEST MVR FC evaporator. URL: https://condorchem.com/en/evaporators/envidest-mvr-fc/ (data of access: 24.03.2025).

$$Q_{concentrate} = Q_{feed} - Q_{distillate} = 24.486 - 2.449 = 22.037 \text{ m}^3\text{/hr.}$$

The salt content in the resulting crystallizer concentrate will be:

$$C_{concentrate} = \frac{1}{(1-R)} \cdot C_{feed} = \frac{1}{(1-0.1)} \cdot 2363.67 = 2626.3 \text{ g/dm}^3.$$

Thus, the total amount of freshwater obtained during the treatment of highly mineralized mine water in the reverse osmosis unit in the evaporator and crystallizer will be:

$$Q_{distillate}^{full} = 667.81 + 791.724 + 2.449 = 1461.983 \text{ m}^3\text{/hr,}$$

which is about 98% of the total amount of mine water received for treatment.

The amount of solid product obtained by implementing the proposed ZLD technology will be 57875.8 kg/hr (57.9 t/hr).

The balance sheet of the process of desalination of highly mineralized waters of mines of the Southern group of the Kryvyi Rih iron ore basin using the proposed ZLD technology is shown in Fig. 6.

Fig. 6. Balance sheet of the mine water desalination process using the proposed ZLD technology

When determining the electricity required for the reverse osmosis process, the amount of distillate formed during the desalination process (667.81 m^3/hr) and the specific electricity consumption per 1 m^3 of freshwater obtained are taken into account, the average value of which is taken to be 3.5 kWh/m^3. Hence, the total amount of electricity required for the reverse osmosis process will be 2337.335 kWh.

When determining the electricity required for the reverse osmosis concentrate evaporation process, the amount of distillate formed at the evaporator outlet (791.724 m^3/hr) and the specific electricity consumption per 1 m^3 of freshwater obtained are taken into account, the value of which for an evaporator with MVR and forced circulation is 48 kWh/m^3. Hence, the total amount of electricity required for the reverse osmosis concentrate evaporation process will be 38002.752 kWh.

When determining the electricity required for the crystallization process of the evaporator concentrate, the amount of distillate produced at the exit of the crystallizer (2,449 m3/hr) and the specific electricity consumption per 1

m^3 of freshwater produced are taken into account, the average value of which for this type of crystallizer is 64 kWh/m^3. Hence, the total amount of electricity required for the crystallization process of the salt mixture will be 156,736 kWh.

Thus, the total amount of electricity required for the desalination process when implementing the proposed ZLD technology for processing highly mineralized wastewater for the Southern group of mines of the Kryvyi Rih iron ore basin will be 40,496.823 kWh.

For the floating solar installation, it is proposed to use highly efficient photovoltaic modules based on advanced monocrystalline technologies with a nominal power of 660 W[14]. Hence, the total number of solar panels will be close to 61,360 pieces.

The panel is characterized by high resistance to adverse weather conditions (withstands wind gusts up to 23 m/s; resistance to wind load of 2400 Pa and snow load – up to 5200 Pa; protection against hail), thanks to which it works even in extreme conditions.

The efficiency of the solar module is 24.4%. The power degradation in the first year of operation will be $<1\%$, the annual power degradation from 2 to 30 years is 0.35% (after 30 years of operation, the guaranteed power will be 88.85%), which guarantees long-term and efficient operation throughout the entire service life. Solar panels are operated in a wide temperature range from -40 to +85°C.

The length of one photovoltaic panel is 2.382 m, the width is 1.134 m. Hence, the area of one solar panel is 2.7 m^2. In this case, the total area occupied by the floating solar installation will be 165668.821 m^2 or 16.6 hectares.

The area of the water mirror in the mine water storage pond located in the Svystunov beam, with the recommended maximum filling level of 86 m, is 145 hectares. Thus, the area occupied by the floating solar installation installed on the artificial reservoir of the Kryvyi Rih Iron Ore Basin will be approximately 11.5% of the total area of the water mirror.

Thus, the implementation of the proposed ZLD technology allows desalinated water that meets environmental safety standards and crystalline NaCl salt to be obtained, which can be used as a valuable raw material for the needs of the national economy. In addition, the installation of a floating solar installation on an artificial reservoir of the Kryvyi Rih iron ore basin will allow us to abandon the use of traditional energy sources for the processing of highly mineralized mine waters using the proposed ZLD technology. This will eliminate the need to purchase energy resources, which are constantly

[14] LONGi Solar Technology 625-660 Wt BIFACIAL Hi-MO 9 LR7-72 HYD. URL: https://surl.li/nztubx (data of access: 20.03.2025).

increasing in price and will contribute to the decarbonization of the energy sector.

CONCLUSIONS

Nowadays, humanity is facing a shortage of freshwater due to its salinity and brackishness. Distillation and membrane processes have been common practice for many years to obtain freshwater Regardless of the technology used for desalination, the disposal of brine and its environmental impact are major concerns. The exponential growth of desalination plants is prompting the search for and implementation of alternative sustainable technologies for the disposal of the growing amount of waste.

Zero Liquid Discharge (ZLD) is one such concept of freshwater production using desalination technology, which is an alternative to all existing brine disposal methods.

Implementing the proposed ZLD technology on the example of the Southern group of mines of the Kryvyi Rih Iron Ore Basin will allow obtaining up to 98% of freshwater during the processing process with its subsequent possible use for agricultural needs (irrigation). The obtained 2% of the solid product in the form of crystalline NaCl salt can be used in any industrial application.

In addition, reducing energy needs and, thereby, increasing the sustainability of desalination systems that are part of the ZLD technology can be achieved through the use of solar energy. For this purpose, it is proposed to install a floating solar installation on a mine water storage pond, the area of which will be approximately 11.5% of the total area of the water mirror of the artificial reservoir.

Thus, ZLD technology will allow enterprises of the Kryvyi Rih Iron Ore Basin to achieve zero wastewater discharge into surface water bodies. Moreover, it is a potential source of cost savings and additional profit. On the other hand, solar energy can play a significant role in meeting the energy needs of ZLD systems, without leaving any harmful impact on the environment.

SUMMARY

One of the main threats to Ukraine’s national security is the irrational use of water resources and the deterioration of ecological state of water bodies. Mineral extraction leads to catastrophic technogenic changes in ecosystems, which negatively affects the biosphere functions including water cycles. The current ecological state of surface water bodies of the Kryvyi Rih Iron Ore Region, the territory of which belongs to the zone of extreme technogenic pollution due to mining activities, has been assessed. The surface waters of the Inhulets and Saksagan Rivers within the Kryvyi Rih Industrial District

have practically lost their natural capacities and properties under the influence of the continuous discharge of saline waters from mining. To manage flows with a high degree of mineralization, it is proposed to implement Zero Liquid Discharge (ZLD) technology using renewable energy sources, which makes the desalination process completely sustainable and environmentally friendly. The parameters of the implementation of the proposed ZLD technology for processing highly mineralized mine waters are substantiated using the example of the Southern group of mines in the Kryvyi Rih Iron Ore Basin. The proposed technology will allow obtaining up to 98% of freshwater during deep processing with its further possible use for agricultural needs and up to 2% of a solid product in the form of crystalline salt, which can be used in any industrial application. The implementation of ZLD technology will contribute to sustainable water use, reduce the load on natural water resources and increase the efficiency of production processes.

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