

# ENVIRONMENTAL PERFORMANCE OF PADINA SETTLING BASIN

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#### Abstract

There is a wide variety of production processes that require large amounts of water. Some of them generate large amounts of wastewater. If these waters are heavily loaded with undissolved substances, they need to be fed to a sedimentation facility before discharging into a surface water intake. The study analyzes the condition and ecological performance of the Padina settling basin, which has been in operation since 1974. For many years, global producers of soda ash, nitrogen and phosphorus fertilizers have been discharged waste water into it, but in addition them, settling basin accepts cinder, slag, ash and waste from water treatment from heat energy production. Cleared water flow from the facility is discharged into Provadiyska river.

Keywords: settling basin, ecological performance.

### **INTRODUCTION**

Each production requires the appropriate raw materials, auxiliary materials and fuels. The obligatory raw materials used in each production process are water and electricity. Global producers with a capacity of millions tons of production per an year use large water amounts. Depending on the applied production processes, one part of water is used in the production, another part is used in a closed water cycle, but a third part - the industrial wastewater is discharged by the enterprises in the surface water bodies. In chemical production, wastewater is more or less loaded with pollutants that can be harmful to aquatic ecosystems. In order not to pollute water bodies, more and more enterprises are building their own wastewater treatment plants. However, this is not enough in some industries, such as soda production, which saturates used water with undissolved substances. In order to remove these substances from the effluent, facilities (stations, basins, artificial lakes, dams) are built, in which a sedimentation process takes place as a subsequent water treatment and only then these waters are discharged into the surface water intakes.

For unimpeded implementation of production processes in Devnya industrial complex, an installation for storage and warehousing of waste from the soda ash production plant Solvay Sodi AD is built. In 1974 the Padina settling basin, located near Padina village, Devnya Municipality (North-eastern planning region of Bulgaria) is put into operation [1, 2, 4, 7].

Therefore, paper presents an overview and analytical review of the existing Padina settling basin (PSB). Study is aimed at analyzing and determining the advantages of Padina settling basin for industrial sites, human health and environment, as due to the large industrial production, Devnya Municipality is defined as an ecological "hot point" in ecological terms [1, 2, 4, 5].

For territories with a large concentration of production enterprises, which have great economic importance, it is especially convenient to create a settling basin so that surface water bodies, which are water intakes of wastewater, to not be affected by enterprises production activity.

Nowadays, for each company, its environmental performance is extremely important, as good environmental performance further expands the markets in which it can operate. In this regard, a facility such as Padina settling basin is of key importance. Maintenance and enlargement of Padina settling basin is of key importance for Northeastern Bulgaria economic development, as it ensures wastewater subsequent purification of the largest soda ash plant in Bulgaria and Europe (Solvay Sodi AD), in compliance with all modern norms and requirements regarding to environmental protection.

### MAIN FEATURES AND ECOLOGICAL PERFORMANCE OF PADINA SETTLING BASIN

The study presents an overview and analytical review of the condition of Padina settling basin of Solvay Sodi AD, which is the study object. Installation is located on the RIEW-Varna territory of and Basin Directorate "Black Sea Region". In addition, its environmental performance is assessed, as since the facility's inception, it receives industrial wastewater loaded with undissolved substances (total nitrogen, total phosphorus, total organic carbon) from several large enterprises.

Installation (including its maintenance and enlargement) is considered. In addition, ways in which it affects environmental components are studied. Collected and analyzed data is from own environmental monitoring of Landfill for non-hazardous waste - Slag-slurry dump "Padina" and Solvay Sodi AD and from their Annual Environmental Reports for the period from 2010 to 2019. [1,2, 3]

Padina settling basin is established (1974) as Slag-slurry dump "Padina" of Solvay Sodi AD. It is a single-section facility of dam type I class. Facility is used for on-site disposal of sludge formed as a result of reactions and gravity sedimentation of wastewater from productions of Solvay Sodi AD and Agropolychim AD, and of waste (cinder, slag, ash and waste from water treatment) transported by hydro transport from termal power plant (TPP) Deven AD. The clarified mixed wastewater stream in Slag-slurry dump is discharged into Provadiyska river. Facility operates in continuous mode throughout the year. Since 2000 TPP is part from Solvay AD.

As a result of the facility use by three industrial enterprises (Solvay Sodi, Agropolychim and TPP Deven) the site is received the status of a landfill for non-hazardous waste – Slag-slurry dump. Agropolychim AD terminated the facility use from 01.12.2011. From 01.01.2015 Solvay Sodi AD is allowed to use wastewater from the thermal power plant wastewater from Chemical Water Treatment Sector, railway unloading for reagents and reagent farm, only for neutralization and cooling of wastewater from electrostatic precipitators to lime kilns. As a result, since 2015 facility is renamed Settling basin Padina, as it receives industrial waste liquids from water demineralization process from sludge pumping section of Solvay Sodi and wastewater from hydrotransport of cinder and ash and from water treatment from TPP Deven. Since 2017 the TPP is merged into Solvay Sodi.

Currently, Padina settling basin receives industrial wastewater from Solvay Sodi AD and receives in transit wastewater, which transports waste from solid fuel combustion from the thermal power plant. Facility is used for mechanical treatment of wastewater and for on-site disposal of the sludge thus formed. The total surface of settling basin is 2,033 6 dka, and of the waste body - 1,750 dka. Settling basin enclosing dam is a rockembankment with a crest length approximately 3 300 m, which is built-up and filled-up gradually, in stages: I, II, III, IV and V stage (up to elevation 47,0 m); VI stage from elevation + 47,00 m to elevation + 51,5 m (medium elevations). After the construction of the Fifth Stage dam (37 m total height and 38 million m<sup>3</sup> volume of disposed sllime) in 2011, stability analyses are made to identify opportunities for further dam height increase. It's concluded that it is possible to be done at two stages by consecutively building of two new enclosing dams (each 5 m high). They will provide additional 17 million m<sup>3</sup> volume for wastes disposal. The Sixth stage upgrading dam construction (up to elevation 52) is started in 2008. As of the end of 2015, facility has 42 m height and 38,106 m<sup>3</sup> deposited slime volume. Rock fill of the VI stage dam is placed directly on the disposed slime, with an offset towards the lake (from the main dam) varving from 0 to 50 m, as it is laid on geomeshes in combination with geotextile and a layer of graded rock. [3, 8]

Padina settling basin maintenance and enlargement are of key importance for Northeastern Bulgaria sustainable development, observing all modern norms and requirements regarding the environment protection.

Atmospheric air: Only ammonia is emitted into the atmosphere from Padina settling basin (NH<sub>3</sub>). The data for the period from 2010 to 2014 is presented in Figure 1.



Fig. 1. NH<sub>3</sub> emissions

For the period 2010-2011, part of these emissions is also due to Agropolychim, whose wastewater from nitrogen and phosphate production lines is accepted into the facility. For period from 2015 to 2019 there is no data for ammonia indicator, because the emitted quantities from Padina settling basin are part of the total reported amount of ammonia emissions, which is calculated according to the internal company methodology of Solvay Sodi balance of ammonia. perform The to methodology takes into account: ammonia emissions from point sources; the amount of ammonia emitted as fugitive emissions; ammonia losses with the product; ammonia fumes from Padina settling basin.

ambient air Regarding to pollutant ammonia (NH<sub>3</sub>) emitted by the installation (threshold = 10 t/y) [6] shows significant exceedance of granted by the International Plant Protection Convention (IPPC) permits, although in different years there are lower and higher measured values. For the study period, the recorded maximum of 851,54 t/y NH<sub>3</sub> is in 2010. This is due to the intake of Agropolychim wastewater from, which continues also in 2011, for that year values of NH<sub>3</sub> 788,29 t/y are reported. As soon as Agropolychim stopped operating the settling basin (2012), NH<sub>3</sub> emissions decreased significantly to 499,54 t/y, but nevertheless values exceeded the norm (threshold = 10 t/y) by almost 50 times. Over the next two years, the reported values rise again. Despite the enormously exceeding of admissible norm throughout studied period, the graph registers a downward trend by reporting values of 611,86 t/y for 2014.

Wastewater and protection of surface water intakes: Until 2011 Agropolychim discharged wastewater from nitrogen and phosphate production lines in Padina settling basin. To 2015, TPP discharges wastewater from the hydro transport of cinder and ash and from the water treatment again in this facility. Since 2015, Solvay Sodi (already receiving wastewater from the thermal power plant) as an owner of the installation performs its own monitoring of wastewater mixed flow (industrial, cooling and rainwater from soda ash and sodium bicarbonate productions) discharged into Provadiyska river. Sources of the three wastewater types are: industrial from distillation, brine cleaning, lime kilns, lime quenching; cooling - from cooling the gas from lime kilns; rain - from the territory of the production site. Treatment plant for part of a mixed wastewater stream is Padina settling basin. Provadiyska river is the water intake of the clarified water discharged from the installation. Monitoring of industrial wastewater monitors harmful substances emissions in them. Table I presents indicators, emission limits and monitoring frequency for sampling point № 2, which refers to Provadiyska river.

TABLE I. Indicators, individual emission limits and sampling frequency for sampling point № 2, Provadiyska river

Indicators	Individual emission limits	Sampling frequency
pH	8,5 - 11,5	Daily
Undissolved substances	100 mg/l	Weekly
Ammonium nitrogen	20 mg/l	Weekly

For sampling point  $\mathbb{N}_{2}$  1 (1002) Drainage channel from Padina settling basin, according to the Complex Permit (CP), in addition to indicators mentioned in Table I wastewater flow is continuously monitored (Table II).

Clarified wastewater quantities discharged from the facility into the river are measured through installed flow meters. The settling basin operator monitors the parameter "Content of undissolved substances in effluents" and ensures that the optimum value is less than 100 mg/l per week. Results of own monitoring of the indicators are documented and keep records. Data from the measurements of Padina settling basin outlet with respect to emissions of harmful substances into the water (total nitrogen, total phosphorus and total or-

ganic carbon) according to EPRTR and PRTR together with the respective threshold quantities are presented in Figures II, III and IV. The total nitrogen amount is determined on the basis of measurements on indicators of ammonium nitrogen, nitrite nitrogen and nitrate nitrogen. The total phosphorus amount is determined on the basis of orthophosphate concentration measurements. The "total organic carbon" concentration is calculated on the basis of measurements taken every two months.

TABLE II. Emission limit values (ELV) for different wastewater flow rates per sampling point № 1 (1002) drainage channel from PSB

Wastewater flow rate		ELV, according to CP
- Q average per day	m <sup>3</sup> /24h	108,02 x 10 <sup>3</sup> m <sup>3</sup> /24h
- Q maximum per hour	m <sup>3</sup> /h	5978 m <sup>3</sup> /h
- Q average per year	m <sup>3</sup> /y	38,860 x 10 <sup>6</sup> m <sup>3</sup> /y

The situation regarding the indicator Total discharged with nitrogen the clarified wastewater flow in the Provadiyska river is not good (Figure 2). Throughout the studied period from 2010 to 2019, the reported quantities exceed many times the limit value, which is 50 t/y. In 2010 and 2011, when Agropolychim AD still exploits the facility, the readings are 611,38 t/y and 542,77 t/y, respectively, which is more than 12 times

increasing the permissible amount of emissions. For the next eight-year period, the readings decreased significantly, with the lowest reported value being in 2014 - 253,76 t/y, which is five times again above the permissible quantity. Trend for the indicator Total nitrogen discharged with the wastewater from Padina settling basin is for excessive quantities, which vary from 294,81 t/y (2016) to 371,60 t/y (2018). This is due to the fact that the operator (world producer of soda ash and sodium bicarbonate) uses almost entirely the annual production capacity, according to CP.

With the indicator Total phosphorus the situation is very good, because by ceasing the use of settling basin by the fertilizer plant, the values of this pollutant in the discharged wastewater get into the set norm (5 t/y). For the analyzed ten-year period, there are exceedances for Total Phosphorus in 2010, when the maximum for the period is reported (6,25 t/y)and in 2011 - 5,63 t/y. In 2012, the readings decreased to 3,69 t/y, and from 2013 to 2019 the reported quantities are around 1,5 t/y. The minimum value is reported in 2016 - 0,81 t/y. After the drastic reduction of the water load with total phosphorus, the tendency of its quantities not to exceed 2 t/y is preserved.



About indicator Total organic carbon for 2010 there are no data reported in the Annual Report on the Environment of Landfill for non-hazardous waste - Slag-slurry dump "Padina". Maximum for the period is reported in 2011 - 788,3 t/y, which is almost 16 times above the norm. Over the next two years, the reported values gradually decreased: 2012 -688,1 t/y and 2013 - 593,84 t/y. This downward trend is confirmed in 2014, when quantities of Total Organic Carbon of 64,13 t/y are registered in the discharged wastewater in Provadiyska river. This is 14,13 t/y above the permitted limit value (50 t/y). In the rest of the





studied period, the readings range from 8 to 23 t/y above normal. The minimum (58,38 t/y) is reported in 2019, which gives reason to believe that soon this indicator will fall within the statutory limits.

Soil and groundwater monitoring: Solvay Sodi is developed a comprehensive plan for monitoring soils and groundwater. In 2009 Solvay Sodi performs an analysis of the condition of the soils (ie determines the base condition) of the territory on which its facilities are located, in the permanent monitoring points according to the required indicators. The analyzed soil samples are selected from the surface layer 0-20 cm, which is most exposed to meteorological and other external factors (anthropogenic impact through fertilization of autumn and spring crops; the presence of high groundwater, helping the transfer of salts from saline areas close). The points that are directly related to PSB, object of the study, are:

- point  $N_{2}$  1 - opposite the exit of PSB (point 1017);

- point  $N_{2}$  – to the drainage channel (point 1016);

- point  $\mathbb{N}_{2}$  3 – to the Padina village (point 1018);

- point  $N_{2}$  4 – in the eastern part of Trastikovo field (point 1019);

- point No 5 – 100 m from drainage channel gratings of "Padina" in a westerly direction (point 1020).

The indicators that are monitored are: pH, specific electrical conductivity (SEC), dry residue,  $CO_3^{2-}$  (carbonates),  $HCO_3^{-}$  (bicarbonates), chlorides, sulfates, calcium, magnesium, phosphates, nitrates.

Monitoring analyzes show a significant improvement of soils condition compared to the determined baseline condition. This is also the case for groundwater. Own groundwater monitoring is performed at the following sampling points for PSB: Piezometer № 10, Piezometer № 16 and Piezometer № 17. The indicators that are monitored are: water level. active reaction pH, total hardness, ammonium chlorides, phosphates, iron, copper, ion. chromium, zinc, arsenic, cadmium, mercury, nickel, lead, sulfates, nitrate ions, nitrite ions, electrical conductivity, sodium, magnesium. Monitoring frequency is once a year, except for heavy metals for which the monitoring is performed once every five years. From the conducted monitoring it is established that there are no deviations of the observed indicators from the baseline condition. The good results in terms of soil and groundwater status are result of periodic inspections for leaks from pipelines and equipment located outdoors. The sludge pipes are checked daily. In the presence of leaks, the causes are identified and eliminated as soon as possible.

Waste recovery and disposal: Until 2014 Padina settling basin, until then the so-called Landfill for non-hazardous waste - Slag-slurry dump "Padina", acceptes for disposal the waste groups listed in Table III:

TABLE III. Disposed waste groups

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Waste name and enterprise that submits it for disposal	Code		
Sludges from on-site effluent treatment, other than those mentioned in code 06 05 02 – Solvay Sodi	06 05 03		
Cinder, slag and bottom ash from boilers (excluding boiler ash referred to in 10 01 04) – Deven	10 01 01		
Entrained fly ash from burning coal - Deven	10 01 02		
Solid wastes from calcium-based reactions from desulphurisation of waste gases (a waste from low-sulfur coal and limestone using) - Deven	10 01 05		
Sands of combustion in a fluidized bed - Deven	10 01 24		
Solid wastes from initial filtration and from sieves and screens - Deven	19 09 01		
Sludges from decarbonation - Deven	19 09 03		
Solutions and sludges from regeneration of ion- exchangers - Deven	19 09 06		

Until 2011 it also accepts waste with code 06 05 03 from Agropolychim. With the cessation of activities for the disposal of all these wastes, with the exception of those classified in group 06 05 03, the status of the facility has been changed from a Slag-slurry dump "Padina" in a settling basin. Since 2015, PSB accepts for disposal only waste with code 06 05 03, which enters the facility through sludge pipelines of Solvay Sodi. For this waste, activities marked with code D9 -Physico-chemical treatment leading to formation of final compounds or mixtures, which are disposed by one of activities with codes D1 to D12 and a disposal operation marked with code D12 - permanent storage in Padina settling basin are permitted.

Waste groups with codes 10 01 01, 10 01 02, 10 01 05 - Solid wastes from calciumbased reactions resulting from desulphurisation of waste gases (waste from the sharing of lowsulfur coal and limestone) and 10 01 24, which are generated from the production activity of Solvay Sodi are utilized for technical reclamation of the retreat between the 5th and 6th stages of upgrading of Padina settling basin. There is a project for partial technical and biological reclamation of the retreat between the dikes of the 5th and 6th stages of upgrading the facility. The recovery activity is marked with code R10 - Tillage, leading to improvements for agriculture or the environment.

In addition to monitoring by components and environmental factors, the body condition of settling basin is also monitored. Geodetic measurements are performed. The shrinkage of the base of dams is measured by a system of devices for measuring the shrinkage degree. Devices for shrinkage degree measuring monitor the vertical deformations at the base of the 5th stage dam. Based on the measurements, the facility operator knows what is the development trend of the process and, accordingly, what life remains on the facility, which operates for almost half a century.

Pipelines to Padina settling basin are being replaced and a new type of compensator is being used. With the implementation of this activity the need for drainage is eliminated and the agricultural lands pollution along the route of the sludge pipelines is minimized. Research and design works are carried out to maintain the dam stability and its upgrade, through which reliable information about the dam is obtained. Facility dam is upgraded, which is necessary for its further use, which provides an opportunity for long-term facility operation until its full capacity is exhausted. Implementation of such activities by the settling basin operator has a positive effect on the life of the facility itself. The company Sweko Energoproject AD, which provides all necessary services related to the design and operation since the facility commissioning, is developed a Preliminary Design for the Seventh Stage of Upgrading; Detailed design for the control and measuring system (CMS) of the dam from the Sixth stage of upgrading; Technical project for construction of a new cell for storage of waste from TPP Deven on the territory of PSB. Through these measures Solvay Sodi ensures the future facility operation until the full depletion of its capacity. In addition, Solvay Sodi proves to the authorities that it undertakes and implements the possible measures and activities in order to comply with the environmental requirements. This is proved in 2017, when Solvay Sodi was recertified in accordance with ISO 14001:2015 requirements, Padina settling basin also, be-cause it is a treatment plant, which is an ex-tremely important part of the entire production process of soda ash from Solvav Sodi.

# CONCLUSION

Presented overview and analytical review of Padina settling basin shows that the operator takes all necessary measures to ensure optimal facility operation. In addition to installation maintaining and upgrading in order to use its full capacity, the operator is constantly striving to improve the applied production processes, as they determine the degree of loading of waste-water with undissolved substances. This is evi-denced by the analysis and trends determination. But in study support also are recertification in accordance with ISO 14001:2015 requirements, as well as the presence of a certified IEMS, according to ISO 14001, ISO 9000, OHSAS 18000 and ISO 45001:2018. Regarding to harmful substances discharges, the general trend is to reduce the surface water intakes load. But there is also soil condition improvement as well as of the groundwater. The most significant problem is reported with regard to ambient air pollution with ammonia, although the trend is downward. Emitted quantities of this pollutant are 10-times above the norm, still. Considering the importance for good economic development of Devnya municipality and respectively entire Northeastern planning region of Bulgaria, responsible institutions refrain from imposing drastic measures against the operator, which demonstrates that will continue to work towards better environmental performance.

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