Environmental state and buffering properties of underground hydrosphere in waste landfill site of the largest petrochemical companies in Europe

2016 IOP Conf. Ser.: Earth Environ. Sci. 33 012019

(http://iopscience.iop.org/1755-1315/33/1/012019)

Environmental state and buffering properties of underground hydrosphere in waste landfill site of the largest petrochemical companies in Europe

R Kh Musin[1], N A Kurlyanov[2], Z G Kalkamanova[3] and T V Korotchenko[4]

[1, 2, 3] Kazan Federal University, Kazan, Russia
[4] Tomsk Polytechnic University, Tomsk, Russia

E-mail: [1]Rustam.Musin@kpfu.ru

Abstract. The article examines the waste landfill site of PJSC “Nizhnekamskneftekhim” built 1982. Particular attention is paid to the volume of disposed wastes and peculiarities of landfill operation. It has been revealed that the landfill negatively impacts groundwater. The increase in groundwater level and contamination degree is dependent on recharge from infiltration of precipitation that interacts with the waste in the landfill cells. Groundwater contamination follows the longitudinal distribution pattern, with maximum intensity reaching in the nearest area of the landfill. With increasing distance, concentration of all pollutants sharply reduces. Within three kilometers away from the landfill, groundwater turns to its background values indicating its quality. The landfill discharges oil, phenols, formaldehyde, benzol, toluene, xylene, ethylbenzene, and iron and, to a lesser extent, sulfates, chlorides and barium into the underground hydrosphere. The overlimiting concentrations of other components are caused by intensive leaching from the rocks by aggressive carbonic acid water. The concentrations of hydrocarbonates can reach 8 g/l in the groundwater within the landfill and its nearest area, however, under natural conditions, they do not exceed 0.4 g/l. This is only possible in a case of partial activity of carbon dioxide associated with destruction of organic matter disposed in the landfill. One of the processes that play an important role in groundwater quality recovery is mixing of contaminated groundwater with infiltrating precipitation.

1. Introduction

PJSC "Nizhnekamskneftekhim» is one of the largest petrochemical companies in Europe specialized in the production of synthetic rubber, plastics, ethylene and other products (more than 100 names). Its annual volume is more than 1.5 million tons and the cost is more than 100 billion roubles. The main production facility of the company includes 10 plants and 7 different departments (Department of Science and Technology, Design, and etc.). The main production facilities are located in the city of Nizhnekamsk, Republic of Tatarstan. The company was founded in 1967. Most industrial waste is dumped in the landfill which has been in service since 1982. By 2014, the landfill capacity has been depleted up to 80%. The landfill holds about 504.080.7 m^3 of waste consisting of different compounds. Identification of the environmental impact of the discussed landfill is a rather critical issue.

2. Objects and methods of research

The area of the waste landfill is 0.25 km^2 (0.5 * 0.5 km). It is located within the Volgo-Ural anteclise of the Russian plate, i.e. Kama-Vyatka artesian basin, on the left bank of the river Kama, near the axis of the forested watershed, 8 km to the south-east of Nizhnekamsk. The altitude above sea level of unbroken surface within the landfill site is 186–199 m, with altitude above riverbed being less than 120 m. The closest settlements are situated at a distance of 3 kilometers, with the population not exceeding 400 inhabitants. The gravity drain is of south-eastern direction. The surface slope is not more than $2–3^0$ (figure 1). The upper part of geological cross-section (200 m) is composed of subhorizontal facies-irregular complexes of carbonate-terrigenous rock (Urzhum and Kazan stage). Within the landfill site, it is represented by Quaternary loam soil up to 2-4 m in thickness and top soil.

The highest recorded stage (160–205 m) is composed of mottled formations characterized by interbedded sandstones and clay, with thickness of definite layers reaching 3-4 m (greater thickness is much more rare). Sandstones are usually polymistic, fine-grained, and weakly cemented. Clay carries thin variously fractured interbeds of siltstone and fine-grained sandstone. The ratio of pelitic and psammitic rocks is about 2:1.

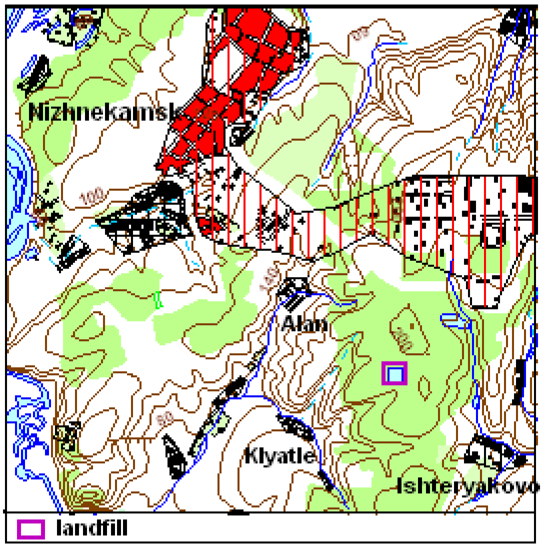

Figure1. The landfill location.

The underlying Kazan sequence (140-160 m) is of the similar structure. Its basement, being 30-40 m in thickness, is composed of grey-colored clay carrying interbeds of carbonate rocks (1-3 m in thickness). In the landfill site, the Kazan sedimentary complex is underlain by the sequence of so-called “lingual clay”, being 14 m in thickness within the hypsometric interval, i.e. 2-16 m. This sequence is extended along the strike and plays hydrogeological role as a regional impermeable horizon.

The groundwater of the described cross-section is interstitial, crevice, and interstitial-crevice. These types form separate aquifers which are basically confined to permeable sandstone and carbonate rocks comprising Urzhum, Upperkazan and Lowerkazan aquifers. The difference in adjacent aquifer levels can reach several meters reflecting the relief of the territory. The groundwater flow is of south-western direction. In addition, downward filtration is identified across the whole cross-section. This explains the fact that some aquifers are hydraulically connected. There no continuous impermeable horizons up to the layer of “lingual clay”. Groundwater is recharged from infiltration of precipitation, i.e. rain and snow. The regular annual precipitation is 554.6 mm. Under natural conditions, groundwater above the impermeable clay layer mostly belongs to hydrocarbonate-magnesium-calcium type (here and further the elements are listed in order of increasing mole-percent concentration), mineralization being 0.2–0.8 g/l and total hardness – up to 7-8 mM/l. Mineralization and hardness increase with depth, however, the groundwater quality meets all drinking standards. Brackish water can be found below the impermeable clay layer within the Ufa stage Sheshminsk deposits.

These specific features of groundwater composition are determined by impact of natural factors, more precisely, interaction of atmospheric precipitation and peculiar types of soils and rocks identified within the cross-section. During the rainless period, the depth of the first aquifer is naturally 3-8 m, with free gravitational waters being located within sandstones and Urzhum stage clays, characterized by the average values of filtration capacity, i.e. 1.23 and 0.05 m/day, respectively. It is a free aquifer with the areas of excessive pressure 0.5–1 m [1] which to be referred to henceforth as ground aquifer.

The landfill site comprises 48 separate waste cells, 50*70 m in size and 3–5 m in depth. The waste cell bottom and walls are made of rammed clay; the walls of outermost eastern waste cells are concreted. Approximately 250 types of wastes of III–V hazard classes (solid, liquid and pasty) are disposed of in the landfill. Mainly, these wastes are catalysts, polymer materials, sediments, oil sludge, pipeline and tank sludge, and etc. The landfill holds about 504.080.7 m^3 of wastes which had been dumped by 2014: solid forms – 444717.9; pasty– 51467.8; liquid – 7895.

The landfill is planned to be reconstructed, precisely, the wastes are proposed to be sealed within a waterproof tank. To develop such waterproof tanks, first of all, it is required to remove the waste from fully filled cells. Then, impermeable screen should be installed on the inside of the tank. The cells are planned to be backfilled with the temporarily removed wastes and sealed with the impermeable screen. Seeding the soil to reintroduce vegetation is the final activity. The impermeable screen is proposed to be of geosynthetic materials characterized by extremely low filtration properties – $(2–5)*10^{-11}$ m/c. Eight waste cells equipped only with impermeable screen at the bottom are planned to be on service.

The interception ditch with pipe drainage has been excavated along the external perimeter of the landfill in order to stop the flow of surface waters and part of ground waters. There are also natural impermeable screen, i.e. a clay fence up to 6 m in depth and 5 m in width along the northern and southern borders of the landfill, and pump station which pumps drainage water and water from the waste cells to the water treatment facilities located outside the landfill site. The whole area is enclosed by a concrete fence 2 m in height. In addition, there is a continuous monitoring of air and groundwater quality. The quality of soil around the landfill site, as well as the quality of surface and ground waters at some distance from the site (near the closest settlements), is also controlled on a schedule basis. Groundwater quality is monitored by means of two observation well networks. The first network which includes 12 wells is located close to the landfill site, while the second one comprising 20 wells is about 150 m from the first monitoring network.

The landfill site has been thoroughly studied. The detailed geo-engineering research was carried out in 1975, 1991 and 2011. The official monitoring of surface and ground surface waters, as well as air and soil quality assessment, is regularly conducted. The geo-engineering research involved monitoring of groundwater level and hydrochemical sampling. In addition, hydro-geoenvironmental research were carried out within the landfill site and outside in 2004, 2011, and 2012. Thus, there are a number of hydroisobath maps made up at different time and various hydrochemical data including the following parameters of groundwater: organoleptic properties, permanganate index, COD, BOD; mineralization, pH, total hardness, $CO_3^{2-,}$ HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, F^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SiO_2; microcomponents: Al, B, Ba, Sr, Be, As, F, Br, Fe, Cd, Mn, Cu, Mo, Ni, Hg, Pb, Se, Zn, Cr, Co; organic substances: petroleum products, phenols, formaldehyde, benzene, toluene, xylene, ethylbenzene, detergents, pesticides (DDT, 2,4-D, γ-HCH; HS); α- and β- activity.

To determine the impact of the landfill on the ground hydrosphere, the authors conducted hydrodynamic and balance calculations using analytical method and modelling approach (Processing Modflow) aimed at defining: intensity of infiltration recharge of groundwater and underlying intermediate water; flow rate of contaminated groundwater in the landfill “outlet”; flow rate of pure groundwater within the second and the third aquifer systems in the landfill “inlet”; efficiency of drainage system. In addition, hydrogeochemical data have been processed.

3. Results and discussion

The data of hydro-geoenvironmental research show that groundwater is increasingly negatively affected by the landfill. During the first decade of landfill operation, there was a rise in groundwater level of about 1 to 5 meters just below the waste cells. The groundwater anionic composition changed from hydrocarbonate to hydrocarbonate-chloride. The increase in groundwater mineralization from 0.2–0.4 to 4–5 g/l was identified. The total hardness changed from 4–8 to 40–70 mM/l. Today, mineralization of groundwater within the landfill and its nearest areas (observation wells of the first monitoring network) can reach 7–12 g/l; hardness can reach 70–135 mM/l; the concentration of the most characteristic pollutants (mg/l) are as follows: petroleum products – up to 500–982; phenols – up to 13.9; total iron – up to 153 (water is mainly of chloride-hydrocarbonate sodium-calcium type). However, the concentrations of most pollutants decrease by one or two orders of magnitude at a relatively close distance from the landfill, i.e. the second monitoring network of observation wells

(Figure 2). According to previous geo-engineering research and environmental investigations, the changes in pollutants concentration were stipulated by liquid waste seepage.

The results of the current research provide the grounds for the following conclusions:

1. The fact that the landfill has become a major source of recharge to the groundwater stipulates the rise in groundwater level within the landfill site. At the same time, it should be noted that groundwater is mainly recharged not by liquid wastes, but by precipitation of different types. Within the landfill site, the over-the-surface flow is disturbed, therefore, most precipitation accumulates (excluding evaporation) within this area. Currently, the intensity of total infiltration within the waste-cell area is 2.8 higher than its standard values, precisely, it reaches 208.2 mm/year (37.5% of normal precipitation). The present water balance within the landfill (m^3/day): inflow (332.75): precipitation – 324.12; liquid industrial waste – 8.63; discharge (332.75): evaporation – 184.69; infiltration – 129.98; runoff – 5.46; pumping from waste cells to the drainage station – 5.05; waste cell flooding – 7.57.

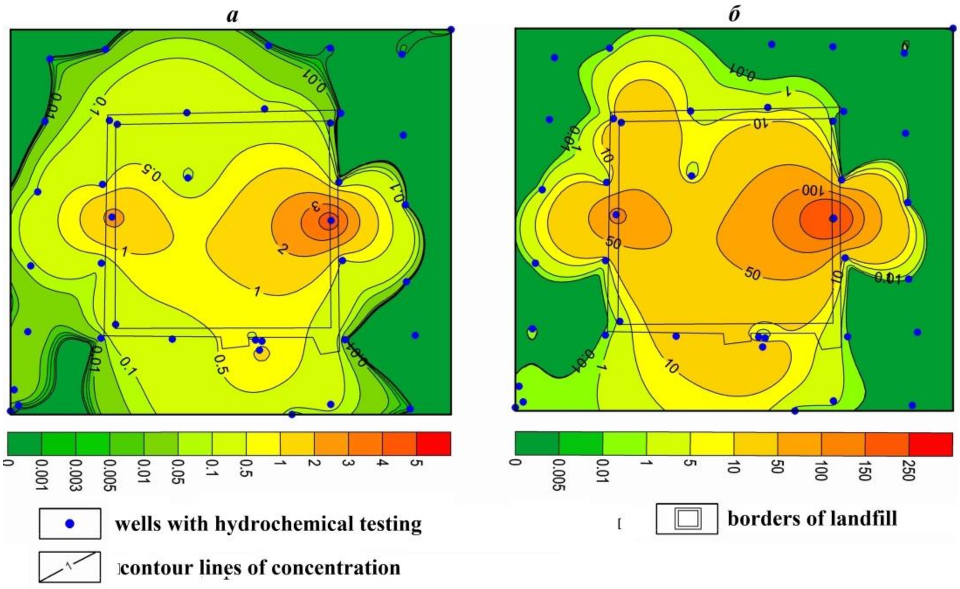

Figure 2. Isoconcentration contour maps (mg/l): phenols (a) and oil (b) in groundwater, sampling data 2011.

2. Groundwater contamination is caused by infiltration and down filtration of precipitation that is altered by waste (to a lesser extent liquid wastes) interaction with water.

3. The flow rate of extremely polluted filtrate through the waste cell bottom is 129.98 m^3/day, including 8.63 m^3/day of liquid waste; the remaining volume is of altered precipitation. In the groundwater flow, the flowrate of filtrate is 121.67 m^3/day (the remaining filtrate volume, i.e. 8.31 m^3/day, recharges the underlying Upper Kazan aquifer system). The total flowrate of groundwater flow is 172.7 m^3/day, including 64.31 m^3/day of water that runs into the underground drainage system. The flow rate of the contaminated ground flow that is not drained is 116.7 m^3/day, including 108.39 m^3/day of groundwater flow and 8.63 m^3/day of deep underground drainage.

4. The landfill wastes can be the reason for the presence of oil products, phenol formaldehyde, benzene, toluene, xylene, ethylbenzene, iron and, to a lesser extent, sulphates, chlorides, barium (high concentrations that 10 times exceed maximum allowable concentrations for drinking water are a specific feature of iron and other highly correlated organic matters). The high concentrations of the above-enumerated elements are basically identified within the waste cell area of the landfill. However, at the distance of 150 m from this area (the second network of observation wells), these concentrations can reduce by factors of 10 and more. The concentration of most inorganic microelements (Al, B, As, F, Br, Cd, Mn, Mo, Hg, Pb, Cr) demonstrates a negative correlation with the distance up to the waste cell area. It should be noted that maximum allowable concentrations can be exceeded in the wells of the first monitoring network, with concentrations of 3-5 being a rare case. This fact can be adequately

explained by intensive leaching both of microelements, and basic cations of mineral matrix by aggressive carbon-dioxide waters with concentration of hydrocarbonate exceeding 800–1000 mg/l (HCO_3^- content can reach 4–8 g/l, while in natural environment it does not exceed 400 mg/l). The hydrocarbonate groundwater is mainly found within the waste cell area of the landfill. This is only possible in a case of partial activity of carbon dioxide [2, 3] associated with destruction (oxidation) of organic matter disposed in the landfill. From the above-mentioned microelements, the presence of F, Br, and probably, As and Hg is stipulated by the disposed wastes, while the rest microelements are held in the cross-section rocks. The landfill operating procedures do not affect the content of nitrates, nitrites, phosphates, fluorides, bromides in groundwater. In addition, the landfill does not alter the content of Co, Cu, Ni, Se, Sr, Zn, Be, as well as synthetic surface active substances and pesticides (DDT, 2.4 D'; γ-HCH; HS).

5. In general, groundwater contamination follows the longitudinal distribution pattern (observation wells located close to the waste cell area would show different groundwater composition). This is due to the fact that each waste cell is designated for dumping a definite type of waste, therefore, each of them is characterized by a peculiar composition of the filtrate. The soil which divides the waste cells demonstrates its own composition of the groundwater. Thus, the groundwater table within the landfill site looks like a “patchwork quilt” in terms of hydrogeochemistry. When separate water currents move in south-western direction as a part of the main ground flow, they can hardly mix, with the boundary water layers being diffused due to lateral hydrodispesion. The low rate of the described processes defines the longitudinal distribution pattern of groundwater contamination.

6. The reduction of groundwater mineralization and hardness, as well as the decrease in pollutant content with increasing distance from the landfill, is caused by various processes and phenomena, precisely, sorption and diffusion, lateral hydrodispesion, pollutant destruction (particularly petroleum products and phenols), precipitation of Fe, Mn, etc. as pH and Eh conditions change. The most significant factor that affects pollutant concentration is natural dilution of contaminated waters with pure waters (in case of south-western filtration, groundwater is recharged from each square meter of the Earth’s surface in volume of 1.9*10-4 m3/day (67.6 mm/year).

7. When landfill filtrates (8.63 m^3/day) reach the upper- and sometimes the lower Kazan aquifer systems, they are also intensively diluted with clean groundwater. Based on the data of geofiltration modeling, the ground flows with the flow rate of 253 and 131 m^3/day recharge the upper and lower Kazan complexes from the eastern part of the landfill, i.e. underground watershed. These data are proved by local and spotted distribution pattern of high petroleum products concentrations in waters of the upper Kazan complex in the southern part of the landfill.

7. The identified processes of “self-purification” are obviously correlated with the fact that composition of ground and surface waters near the settlement Klyatle (at a distance of 3 kilometres from the landfill) demonstrates no significant changes.

8. The local occurrence of groundwater contamination is a characteristic feature of many other industrial waste landfills, with organic matter being dumped. The most vivid examples of waste landfills which have been thoroughly studied are as follows: the Kohtla-Jдrve landfill (Estonia) that was started in 1938 and holds $8*10^7$ m^3 of liquid oil shale mining residues [4]; and closed domestic and industrial waste disposal site in Hamilton (Canada) of 50 ha [5].

References

[1] Musin R Kh and Musina R Z 2014 About the influence of industrial waste landfills to hydrolithosphere *J. Nedropolzovanie XXI* **87–89** 99

[2] Shvartsev S L 1982 “*Osnovyi gidrogeologii. Gidrogeohimiya*” (Basics of hydrogeology. Hydrogeochemistry) (Novosibirsk: Nauka) p 288

[3] Roscoe Moss Company 1990 *Handbook of Ground Water Development* (John Wiley & Sons) p 493

[4] Vallner L, Gavrilova O and Vilu R 2015 Environmental risks and problems of the optimal management of an oil shale semi-coke and ash landfill in Kohtla-Jдrve, Estonia *Science of*

The Total Environment **524–525** 400 – 415
[5] Barker J F, Barbash J E and Labonte M 1988 Groundwater contamination at a landfill sited on fractured carbonate and shale *J. of Contaminant Hydrology* **3** 1–25