# Environmental effect of reservoirs accumulating highly mineralized oil-field waste waters

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## 1. Abstract

The effect of oil-field wastewater (OFWW) storage ponds on grounds, soils and ground waters has been studied for 40 years. 40 years after polluting, chernozems typical show natural desalinization and desolonization processes due to washing water conditions and genetically defined high content of carbonates and gypsum in the soil profile and soil-forming rock. Yet they have an increased content of water-soluble salts, exchangeable sodium and electrical resistance typical for alkali soils and solonetzs. Humus accumulative horizons display a hydrophobic property, as a result of leaching carbonates content, cation exchange capacity, mobile nitrogen and phosphorus content decreases. Pollution of soils by wastewater results in accumulation of toxic elements on areas by far exceeding areas of direct impact.

## 2. Introduction

Oil is a natural deposit and is extracted together with water and natural gas. Oil wastewater is made of formation water and industrial waste water. Formation underground water, that is water extracted with oil, amounts to 80-95% of overall volume of wastewater and thus it defines oil wastewater properties (Gainutdinov and others, 1982).

This water has a number of properties important for ecology. First of all, it has a high mineralization level, prevalence of Cl ions among anions and Na ions among cations. Besides, wastewater is a polyingredient pollutant with high geochemical activity and toxicity (Solntseva, Sadov, 1997). It is mostly composed of gas condensate, diethyleneglycol, mineral soluble compounds and mechanical impurities. Technogenic hydrocarbons content can amount to 260 mg/l (Riabov and others, 1983). With this kind of pollution the main salt "press" occurs primarily in organogenic horizons. The speed and depth of intrusion are considerable (Giliazov, Gaisin, 1997). Necessity often arises to collect wastewater in the so-called storage ponds, particularly at the first stage of oil-field exploitation. These ponds may be a source of contamination of fresh underground waters, grounds and soils.

## 3. Methods

Research was made in Shkapovski oil field where in 1960-1961 a storage pond was built in the valley of the Bazlik river (a left tributary of the Dioma). In the valley bed and left side there were developed delluvial and periglacial clays and loam soils as thick as 10 m. Associated brines (mineralization level 270 g/l) were discharged in 1962-1966.(Abdrakhmanov, 1993).

Ground samples were taken by well drilling, with 5 repetitions, underground waters were taken from natural wells and regime drillings. Soil plots were made 40 years after the pond had been liquidated on contaminated areas and background analogues. Analytical experiments were made by standard methods (Arinushkina, 1970). Mathematical statistics methods were applied for material treatment.

## 4. Results

When building the pond they thought the clay shield to be a reliable isolation and leakage to be insignificant due to poor fluid loss properties of rock. However, in the first year of the pond exploitation (summer of 1963) salinization could be observed below the dam and in the wells previously used for water supply (the village of Bazlik 2 km below the pond), and as a result the pond use was discontinued.

5-6 years after brine discharge was stopped, the salts content in clay sediments under the pond bed (to 2 m deep) made 2000-2500 mg/100g of rock (chlorine 1200-100 mg/100g) whereas mineralization of water extractions from non-salidized clays (on valley slopes) made 40-70 mg/100g (chlorine 1.8-3.6 mg/100g), being of hydrocarbonate sodium and calcium composition.

Retests of the pond bed grounds made 19 years after its liquidation (1984) showed substantial desalinization of clay sediments under the first overflood lands terrace and the pond bed annually flooded by water from melted snow. Total salt amount lowered to 70-90 mg/100g, chlorine amount to 3-10 mg/100g (Abdrakhmanov, 2005).

A new series of experiments were made for finding further changes in the water-salt regime of clay rocks and their exchange-adsorbtion properties in July 1991 and August 1997. Testing was done at the same areas. By that time a further desalinization of rocks occurred with the content of chlorine ion not higher than 3-7 mg/100g, which was close to its background one under natural conditions (3-5 mg/100g). Salt concentration decreased to 370-620 mg/100g (chlorine – to 200-380 mg/100g) on the second overflood lands terrace.

Melted and rain waters were used for washing. In winter water height reached 3-5 meters leading to filtration increase under its bed. By mid-summer minor lakes, covered by oil films 2-3 cm thick remained. The water was fresh (0.31 g/l), of hydrocarbonate sodium-calcium composition. The composition of an adsorbed complex (AC) of clay rocks changed qualitatively as well. Clay bearing beds under the storage pond (after discharge stopped) became solonized as a result of cation exchange processes with oil brines, sodium concentration reached 10-53.5 % of the rock cation exchange capacity (CEC), whereas outside the impact area it was not higher than 2-4%.

It should be noted that a relatively short period (2-3 years) of oil brines effect on clay sediments followed by their long washing by weakly mineralized atmospheric precipitates for 38 years not only greatly changed rock salinity but also led to changes in the composition of absorbed cations. This resulted in the prevalence of bivalent cations: calcium – 76-91.5%, magnesium – 19.5-40%, in some profiles – to 88%. Sodium and potassium concentration made1.3-4.5 %. An increased content (to 9.0-12.5%) of univalent cations remained only in profiles saturated by chloride salts. CEC of clay rocks in intensively washed part of the pond remained low – 16.27-19.69 and 6.68-14.69 mg-equ/100 g. In the terrace part in the absence of intensive salinification and further washing AC capacity value was much greater (28.0-45.3 mg-equ/100g).

Maximum chlorine content made 371 mg/100g with total decrease in salt concentration. It should be underlined that no noticeable fall in oil product content in rocks could be observed throughout the whole period.

The scale of contamination of fresh water, its character and pollutants active period depend on many factors: geological structure (rock sedimentology), water mobility in upper hydrodynamic area, kind and compositon of pollutants, deposit exploitation time and others. The area of salinized fresh water in the oilfield under study makes 500 km.

Long-term testing results of chemical analyses and analyses of ground waters mineralizaton showed their inconstancy. Within the oilfield area there was a gradual decrease in the level of mineralization. Mineralization level dependence on the source flow was often the case: a flow fall was accompanied by the growth of diluted salts concentration and vice versa a flow rise – by mineralization level decrease. The change in a source flow is dependent on atmospheric precipitation, i.e. an interrelation between water chemistry, source flow and hydrometereological factors is noticeable. This connection proves the fact that oil brines penetrate into fresh water horizons by convective-filtrational way, mainly via the zone of suspended water.

Figure 1 shows the observed level of water mineralization in a well 2 km away from the storage pond. As can be seen the curve of water mineralization dependence on the number of years after contamination is an exponent described as $y=10.027e^{-0.0599x}$, $R^2 = 0.928$ with probability of $P>0.95$.

For the first 20 years mineralization level varied in the range of 12-5 g/l and was not the same in different years, while lowering in subsequent years was more gradual and consistent. Thus, greater fluctuations in water mineralization level in the first years at high salt concentration are more dependent on annual precipitation. At concentrations below 5g/l mineralization goes down gradually and is less dependent on annual precipitaton fluctuations.

In springs outside the impact of the pond water mineralization makes 5-7 mg/l. Solving the equation with a quantity y=5mg/l you can get x – number of years for full desalinization of water (126 years after 1974, that is 2100).

(1) $y=ae^{-kx}$

(2) $e^{-kx}=ay^{-1}$

(3) $\ln ay^{-1} = kx$

(4) $x=1/k \ln a/y$

with k=0.0599; a=10.027; y=0.005 – x = 126.

Hence, desalinization of ground waters does not occur until 140 years after the pond liquidation. The prediction is in good agreement with the earlier result (Abdrakhmanov, 1993) about the necessity of triple water cycle in soil ground layer for its desalinization.

Topsoil in the area of the pond is typical carbonatic chernozem. Soils in the profiles one kilometer above and below the pond were not polluted. These are highly humus soils, with the reaction close to neutral, high CEC, with 0.4-0.65% of carbonates content.

Building of the pond led to the degradation of topsoil not only in the bed but also in nearby soils. First of all, they are sure to have been salinized and solonized. 40 years after the pond liquidation the level of residual salinization was not higher than 0.1%, which is indicative of full natural desalinization of the soils. The exchangeable sodium content in the profile varied in the range of 0.7-3.5% of CEC, which means the absence of solonization. At the same time, compared to background soils (profiles 7 and 8), they have three times as much water soluble salts and exchangeable sodium, and in the lower part of the profile the content of exchangeable sodium is close to a threshold value of 5% of CEC. This agrees well with the values of electrical resistance varying in the rate of 100-300 Ohm*m, whereas in uncontaminated soils they are higher than 600 Ohm*m.

Pollution by oil-field waste waters contributed to alkalinization of free carbonates whose content was almost 10 times lower than in background typical carbonated chernozems. This led to some acidification of reaction of soil in profile 2 which was not mixed with lower eluvial horizons. Despite the fact that the number of free carbonates reduced in anthropogenic soils of the pond bed, alkalinization occurred with 9.1 pH in the eluvial horizon at the depth of 62-96 cm, maybe due to residual solonization.

The content of overall humus in upper horizons of polluted soils is almost equal to the background one but in the pond bed it was considerably lower and decreased more abruptly down the profile. Humus accumulative soil horizons under the impact of OFWW show hydrophobic property of aggregates, which worsen their water and nuitrition regimes.The content of mobile phosphorus is 6-15 times lower. In polluted soils available nitrogen is somewhat lower than in background soils, in mixed soils 2-3 times lower. Total phosphorus content varies similar to alkalihydrolizable nitrogen.

On some spots of the pond bed the surface is strongly mazutized, vegetation is absent, water surface in depressions is covered with oil films.

OFWW pollution leads to accumulation of toxic elements on the area by far exceeding the area of immediate impact. These elements accumulated over maximum concentration limit and background values in 1, 2, 3 toxicity classes: Cd, As, Zn, Mo, Cu, Co, Ni, Cr, Sr, V.

The vegetation in polluted areas accumulates toxic elements. Strawberry leaves had Pb, Sr, V, Rb, Ba in concentrations much higher than background ones, milfoil leaves had Cd, Rb, Ba.

So, after 40 years of OFWW impact natural desalinization and desolonization of soils set in. At the same time, they keep an elevated content of water soluble salts, exchangeable sodium, electrical resistance characteristic of salinized soils. Due to alkalinization the content of carbonates and cation exchange capacity decreased, water and nutrition regimes worsened, oil content persisted here and there. This kind of pollution contributes to accumulation of toxic elements in soils and plants.

**Table 1 Physical and chemical properties of soils**

| Horizon, depth, cm | pH $H_2O$ | Dry matter | Humus total | Carbonates, $CO_2$ | Water soluble Na | Na exch. | CEC | N alkali-hydrated | $P_2O_5$ total | $P_2O_5$ avai-lable |
|---|---|---|---|---|---|---|---|---|---|---|
| | | % | | | mg-equ/100g | | | mg/kg | mg/100g | |
| Profile 2-2004 Chernozem typical polluted by OFWW | | | | | | | | | | |
| A10-28 | 6.85 | 0.09 | 10.80 | 0.036 | 0.1 | 0.40 | 34.82 | 124 | 191.2 | 2.14 |
| AB28-52 | 6.40 | 0.12 | 6.19 | 0.072 | 0.1 | 0.40 | 31.93 | 66 | 125.4 | 0.52 |
| B52-90 | 6.40 | 0.08 | 2.81 | 0.108 | 0.15 | 0.65 | 33.67 | 56 | 56.4 | 0.14 |
| Profile 3-2004 Chernozem typical polluted by OFWW | | | | | | | | | | |
| A10-40 | 7.20 | 0.08 | 10.22 | 0.072 | 0.1 | 0.25 | 34.96 | 124 | 188.1 | 1.00 |
| B40-80 | 7.10 | 0.07 | 2.65 | 0.072 | 0.15 | 0.35 | 24.60 | 42 | 56.4 | 0.48 |
| Profile 4-2004 Degradated soil | | | | | | | | | | |
| A10-40 | 7.65 | 0.09 | 6.63 | 0.108 | 0.1 | 0.3 | 26.62 | 140 | 131.6 | 0.57 |
| Profile 5-2004 Degradated soil | | | | | | | | | | |
| A10-40 | 7.85 | 0.11 | 7.45 | 0.072 | 0.25 | 0.85 | 24.63 | 98 | 97.18 | 2.38 |
| Profile 6-2004 Degradated soil | | | | | | | | | | |
| A10-44 | 8.40 | 0.13 | 6.20 | 0.036 | 0.15 | 0.35 | 32.50 | 182 | 116.0 | 1.52 |
| B62-96 | 9.10 | 0.09 | 1.98 | 0.072 | 0.2 | 0.5 | 19.43 | 84 | 69.0 | 2.52 |
| C96-120 | 9.40 | 0.09 | 0.68 | 11.276 | 0.15 | 0.3 | 6.52 | 56 | 128.5 | 9.96 |
| Profile 7-2004 Chernozem typical carbonated | | | | | | | | | | |
| A10-26 | 7.50 | 0.03 | 11.02 | 0.361 | 0.15 | 0.35 | 44.61 | 238 | 172.4 | 14.1 |
| AB46-67 | 7.40 | 0.08 | 4.17 | 0.452 | 0.15 | 0.35 | 35.48 | 98 | 100.3 | 1.9 |
| B67-96 | 7.70 | 0.09 | 3.30 | 0.452 | 0.15 | 0.35 | 33.67 | 56 | 94.0 | 2.38 |
| Profile 8-2004 Chernozem typical carbonated | | | | | | | | | | |
| A10-28 | 7.10 | 0.05 | 9.63 | 0.398 | 0.15 | 0.2 | 46.21 | 238 | 188.1 | 12.48 |
| AB42-70 | 7.05 | 0.07 | 4.50 | 0.361 | 0.15 | 0.2 | 34.66 | 84 | 78.4 | 1.67 |
| B70-100 | 7.35 | 0.08 | 2.10 | 0.651 | 0.15 | 0.2 | 26.99 | 42 | 72.1 | 2.14 |

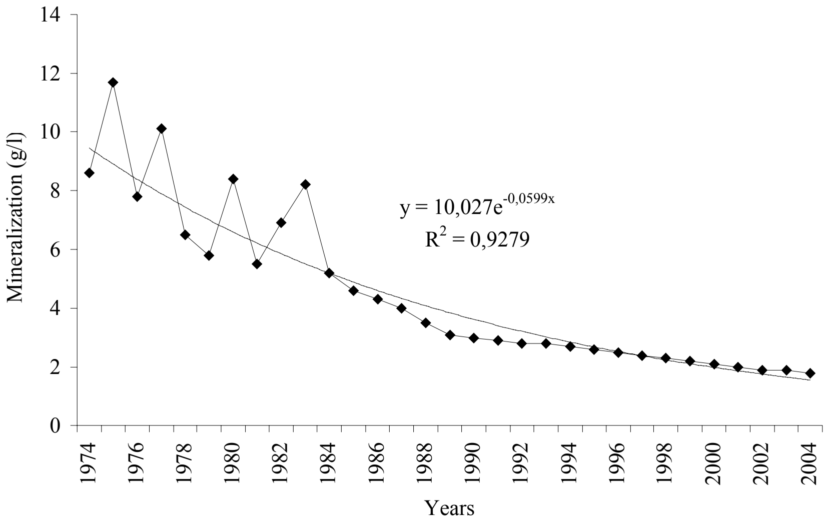


**Figure 1 Dynamics of water mineralization in a spring 2 km away from the pond**

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