JOURNAL OF
ENVIRONMENTAL HYDROLOGY
Open Access Online Journal of the International Association for Environmental Hydrology

VOLUME 24 2016

NUMERICAL MODELING OF THE INTENSIFICATION PROCESSES OF GROUNDWATER TREATMENT FOR HEXAVALENT CHROMIUM USING IN SITU TECHNOLOGY

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The article reports the results of groundwater treatment for hexavalent chromium on the Ilek industrial site located at the Aktobe district in Kazakhstan. This study describes specific techniques, practices, and methodologies currently being employed on sites with the so-called "historical contamination" in Kazakhstan using in situ technology. The goal of this technology is to reduce Cr (VI) in groundwater and contaminated soil to the more thermodynamically stable Cr (III) by creation of reactive zones in the aquifer where migrating contaminants are intercepted and permanently immobilized or degraded into harmless end products. All work is performed by injecting reagent in a contaminated groundwater plume and allowing them to "react" with the contaminants. The main difference of the current work with the standard in situ treatment technology is in creating the so-called hydrocycles when after a period of reagent injection, a phase of water injection that starts to pressurize and enlarge the area of reagent delivery which is then followed by a period of pumping and re-injecting for the further intensification of the treatment process. The process of treatment is controlled based on a numerical model to add or exclude injection wells from the pumping net. Results from chemical reduction experiments on the contaminated zone shows a considerable decrease of hexavalent chromium from 53 mg/L to 0.05 mg/L, indicating that in situ treatment using hydrocycles may be an effective approach when deployed at the field scale. The results of successful treatment are proved by the absence of secondary contamination during three-year monitoring on a site after a period of work performed.

INTRODUCTION

Chromium (Cr) is a heavy metal which has historically been used in a wide range of industrial applications including steel, pigments, wood preservatives, electroplating, metal finishing, dyes, leather tanning, textiles, and chemical manufacture (Papp, John F., 2015). Kazakhstan is on a second place for the chromium production with more than 4 million tons per year (U.S. Geological Survey, 2015). Due to the production at many industrial and waste disposal locations, chromium has been released to the environment via leakage and poor storage during mining or improper disposal practices. Therefore, contamination of soil and groundwater by heavy metal as chromium with high toxicity is a significant problem in the Republic of Kazakhstan (Bekmukhambetov Y.Z. et al., 2014; L. Mueller et al.,2014). In general, the treatment of Cr contamination focuses on the highly toxic hexavalent form Cr (VI) and its transformation into the relatively low toxicity and active trivalent form Cr (III), a process that typically involves chemical reduction and precipitation as Cr (III) (Yin and Allen, 1999, Suthersan, 1997). The purpose of this work, therefore, is to bring together the most current information pertaining to the science of chromium treatment and the process of treatment control on a site during the work based on a numerical model (Nyer and Suthersan, 1996).

BACKGROUND

This treatability study was conducted in response to the recent request from the Ministry of Environment and Water Resources of the Republic of Kazakhstan to evaluate the feasibility of using in situ treatment technologies for chromate reduction and immobilization at the site No. 3, Ilek Industrial Zone, Aktobe district, Kazakhstan. Contamination was initially detected in 1957, soon after the start of Aktobe Plant of Chromium Compounds. The results of observations carried out by a specialized monitoring network showed that during the next 50 years of chromium production forms huge hexavalent chromium plume around the plant's industrial sites. Pollution area reached 14 sq. km with a maximum chromium content reaching 3657 mg/L in an ash drain water ponds, 320 mg/L in the site near plant, and 53 mg/L on the pilot treatment site on a distance of 13 km in comparison with the maximum available by the standards 0.05 mg/L (Rykhluk T.N. et al., 2009).

From slurry ponds and industrial sites chrome moves downstream towards the river bed and in wells located along the river (Pavlichenko L.M., et.al, 2008). Contaminated surface water is a potential threat for public health and may have toxicological poisoning from plants, cattle grazing or by swimming in the river. A recent survey (Bekmukhambetov Y. Z. et al., 2014) shows that technogenic pollution of the environment by chromium and its compounds directly impacts on adults and children's health. Deterioration of medical and demographic determinants, the onset of disability and the morbidity rate in the population residing in this region are directly connected to the harmful effect of chemical substances among which chromium is the primary factor. Chromium, by entering the body from different environments causes essential disbolism and imbalance in the immune system, which in turn affects the state of the disease and further progression of numerous complications.

Assuming the fact that Ilek is a transboundary river is a serious signal for starting treatment actions on the site. The result of feasibility study reveals three sites for treatment. Site number three has an area of 0.8 sq. km (Figure 1) and was used as a pilot due to its relatively low chromium concentration and simple hydrogeological conditions. The whole study and all results are shown for this site.

GEOLOGICAL AND HYDROGEOLOGICAL CONDITIONS

It was necessary to conduct geological and hydrogeological studies to estimate aquifer properties (porosity, conductivity etc.) to quantify reduction processes and determine appropriate amendments to stimulate these processes. The work area Ilek industrial site resides on the north-western part of Kazakhstan on the edge of Aktobe city which is located on the western bank of Ilek river. Geomorphologically, it is a flat alluvial valley. Results of this work reveal the following hydrogeological units (Table 1, Figure 2).

Table 1. Hydrogeological units on the area of contamination

Age		Name	Symbol	Lithology and Thickness	Note
Cainozoic	Quaternary	Upper-Quaternary - Modern alluvial aquifer	aQ_{III-IV}	Boulders, pebble gravel, sand interbedded with loam. Thickness from 5.0-10.0 to 20-40 m	Widespread in the area. Non-artesian. Aquifer hydraulically connected to the surface water of Ilek river. In a low-flow period hexavalent chromium draining to the river. Ground water is not used because of a high contamination rate. Groundwater mineralisation is 4-6 g/L, closer to the river 1.3-1.6 g/L. Mineralization and chemical compound formed due to chemical pollution.
	Tertiary	Miocene-Lower Quaternary aquifer	N_2^3-Q_I	Lens of sand and gravel in clay mass. Thickness is 10-15 m	Locally present. Non- artesian. Groundwater mineralisation is 2,9 g/L. Brakish waters are not used. It is a local aquitard in most of the area.
Mesozoic	Cretaceous	Lower-Cretaceous goterivian aquifer	K_1g	Sands interbedded with clayey and silty deposits. Thickness is 1.5-4.0 m	Non-artesian. Ground water mineralisation is 0.7-6.3 g/L. Low water productivity. Brackish groundwaters are not used.
	Jurassic	Middle-Jurassic aquifer	J_2	Sand, gravel less sandstones. Thickness is 1.5-50.0 m	Artesian. Ground water mineralisation is 1.3 g/L.
Palaeozoic	Permian	Upper-Permian aquifer	P_2	Fractured sandstones. Thickness not studied	Low water productivity. Ground water mineralisation is 1.1 g/L.

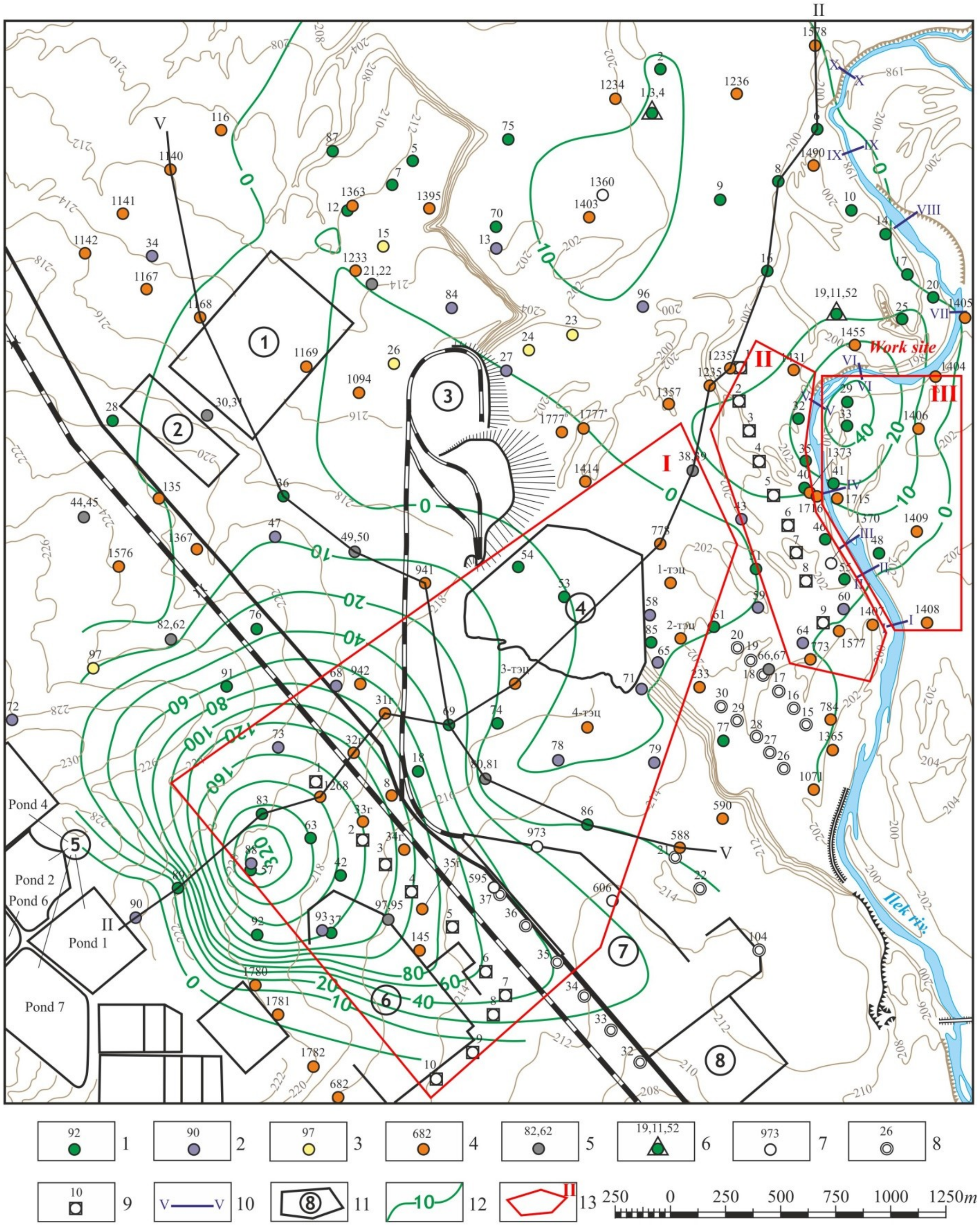

Figure 1. Map of hexavalent chromium contamination, Ilek industrial site, dated 01.01.2011. (Source: Kalitov D.K., Burakov M.M. et. al., 2013).

(1 - exploratory well (borehole); 2 - marking well; 3 - sounding well; 4 - monitoring well; 5 - well cluster; 6 - additional wells for estimation of migration properties of the aquifer; 7 - boreholes for other purposes; 8 - producing well; 9 - drain wells; 10 - gauging stations on Ilek river; 11 - potential sources of contamination (1 -filtration fields; 2 - petroleum storage depot; 3 - slag disposal; 4 - ash disposal; 5 - ash drainwater ponds; 6 - 8 - industrial sites; 9 - isolines of hexavalent chromium concentration, figures - chromium concentration, mg/L; 13 - treatment site.)

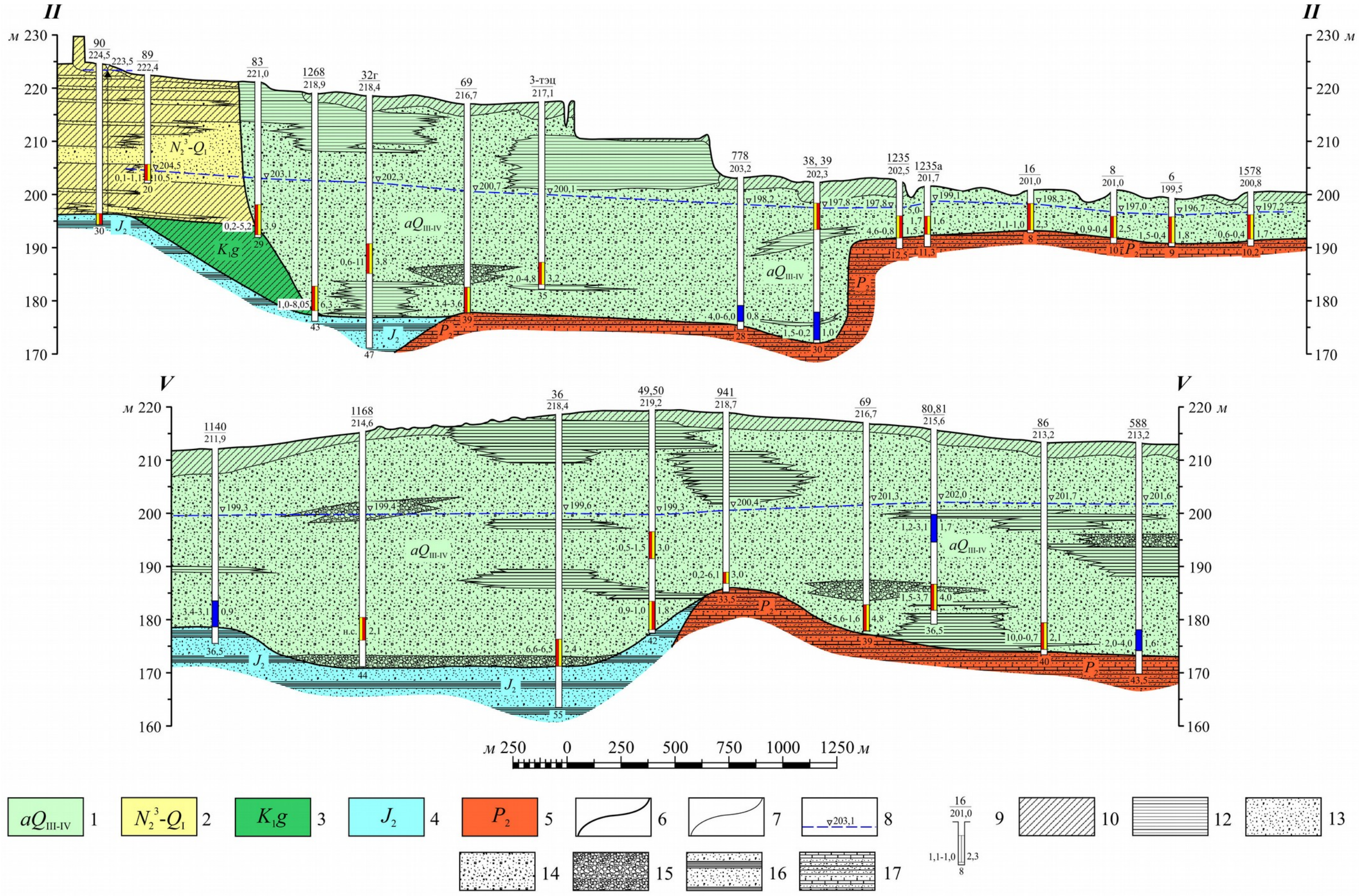

Figure 2 . Hydrogeological cross-section.

Legend: 1-5 – hydrogeological units (1 – Upper-Quaternary Modern alluvial aquifer. Sands and lens of loams; 2 – Miocene-Lower Quaternary aquifer. Clays and lens of sands; 3 – Lower - Cretaceous goterivian aquifer. Interlayers of sands and clays; 4 – Middle-Jurassic aquifer. Sands and lens of clays; 5 – Upper-Permian aquifer. Sandstones, limestones in clays); 6 – border of hydrogeological units; 7 – border of lithological units; 8 – groundwater level. 9 – Borehole. Figures: Overhead in the numerator – well number, in the denominator – well head abs. m.; To the left first – production, L/sec, second – drawdown, m; to the right – groundwater mineralization, g/L; below – well depth, m. Filling corresponds to chemical compound of groundwater; 10-17 – Lithology (10 – loam; 12 – clay; 13 – sand; 14 – sands with gravel and pebble; 15 – gravel and pebble; 16 – layers of sand in clays; 17 – sandstones and limestones in clays). Source: Kalitov D.K., Burakov M.M. et. al., 2013

MATERIALS AND METHODS

Geochemical study

Under oxidizing conditions, the dissolved chromium exists in the form of water-soluble (aq) Cr^{6+}. The real connection is a hydrogen chromate ion $HCrO_4^-$ (pH below 6.5), or chromate ion CrO_4^{2-} (pH above 6.5). Under redox potential (Eh) less than 400 mV chromium exists in a from of Cr^{3+}. In the pH range of normal values (pH ranges from 6 to 11) water-soluble Cr^{3+} precipitates as a solid $Cr(OH)_3$. At lower pH values water-soluble Cr^{3+} may exist as $Cr(OH)^{2+}$(DEFRA, 2002). Therefore, most of the in situ schemes based on the reduction of active anion Cr^{6+} up to Cr^{3+} precipitated in the solid phase and remove chromium from solution. Equilibrium for this process is shown as:

$$HCrO_4^-(aq) + 7H^+ + 3e^- \rightarrow Cr^{3+}(aq) + 4H_2O \quad \text{Standard potential} = 1{,}195\ B$$

The following reducing agents were tested in the laboratory during geochemical study (Korchevsky A.A., Burakov M.M. et al, 2007) on the site:

- sodium dithionite ($Na_2S_2O_4$);
- sodium metabisulphite ($Na_2S_2O_5$);
- sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$);
- ferrous (sulphate) iron (FeSO4·7H2O);
- ferrous (sulphate) iron plus molasses;
- molasses.

Tests with dithionite

A comparative analysis of the tests with dithionite revealed that dithionite reducing agent is impractical for the following reasons:

- large amount of dithionite is necessary for the reaction in groundwater;
- groundwater after the reaction contain high concentrations of total dissolved solids, including sodium sulphate (up to 5,000 mg/L of sulphate for groundwater with 100 mg/L of Cr^{6+} concentration);
- unstable, there are various extraneous reactions;
- the amount of iron available in a solid phase to precipitate which may be reduced to bivalent iron to react with Cr^{6+} is relatively low;
- more than a third of the aquifer should react with dithionite to form a reaction zone for removing all Cr^{6+} from groundwater.

Tests with sodium metabisulphite

Reactions were substantial and have been relatively rapid, but the required amount of sodium metabisulfite increase the total dissolved solids (TDS) in groundwater (with average concentration of Cr^{6+} above 100 mg/L) by an amount in the range from 1,000 to 3,000 mg/L (mostly as sodium sulphate).

Tests with sodium thiosulphate

The reactions were not effective in all cases and it turned out that there are adverse reactions. The required amount of sodium thiosulphate increase the total dissolved solids (TDS) in groundwater (with average concentration of Cr^{6+} 100 mg/L) by an amount in the range of 6,000 to 30,000 mg/L (mostly as sodium sulphate).

Tests with ferrous (sulphate) iron and molasses

Series of tests with ferrous sulphate heptahydrate and molasses (Tests 1, 7, 9 and 12) and no molasses (Test 6) had been conducted (Table 2). For the tests used groundwater with Cr^{6+} concentration ranging from 40 to 100 mg/L and Fe^{2+} used as a reagent with initial concentration from 550 mg/L.

Field studies on a site were conducted for estimating reagent concentrations and aquifer injectivity (water-intake rate). In other words, field studies aimed at assessing volumes of ferrous sulphate (during the field studies used $FeSO_4$·7H2O) necessary for effective treatment of the hexavalent chromium concentration in an injecting well. It was also used molasses with weight concentrations 1-1.5 % during the field studies.

Table 2. Results of test series with ferrous sulphate heptahydrate and molasses

Test	Used reagents	Initial Cr^{6+} concentration in solution		Cr^{6+} removed from solution	Fe/Cr mg Relation
		mg/L	mg	%	
1	Bivalent ferrous iron and Molasses (1,4 %)	130	5,2	100	2,5
2	Molasses (1,4 %)	130	7,8	5	-
3	Tiosulphate (2,4 %)	130	5,2	31	-
4	Tiosulphate (20 %)	130	5,2	83	-
5	Molasses (3,7 %)	130	5,2	81	-
6	Bivalent ferrous iron (6 ml)	130	13,0	100	2,96
7	Bivalent ferrous iron (4 ml) and Molasses (1,4 %)	130	13,0	100	1,98
8	Tiosulphate (50 %)	130	5,2	99.96	-
9	Bivalent ferrous iron and Molasses (1,4 %)	130	NA	-	-
10	Molasses (4,5 %)	130	NA	-	-
11	Molasses (5,1 %)	130	7,8	62	-
12	Bivalent ferrous iron and Molasses (1,5 %)	253/260	7,8	100	3,5

For the aquifer water – intake rate assessment hold injection works. In wells 159 mm in diameter, injected water with measuring volume of water injected and dynamic level. Aquifer water – intake rate by the end of injection works was equal to 3-5 m^3/h (72-120 m^3/day, 0.83-1.38 L/sec) proving high injectivity of the aquifer. Based on the injection works defined, that it is possible to inject a solution equal to 150L/h.

Field studies on selection the most effective Fe^{2+} concentration started from reagent solution preparation in 40 m^3 tanks. Solution compound in each tank was as follows:

- 300 kg molasses (except test 6 see table 2);
- 66 kg ferrous sulphate;
- 19500 L of water.

Estimated Fe^{2+} concentration in the first tank were 730, 690, and 685 mg/L on the depth (0.66m, 1.3 m and at the top or upper edge of the water in the tank) and 745, 785, and 670 mg/L on the same depth in the second tank. In all injection wells with the help of a centrifugal pump packer, average capacity of 50 L/min was fed to the working solution of iron sulfate/molasses with an interval of 1 m at full capacity of the aquifer. Each interval is pumped about 1400 liters of solution.

Formation of the reaction zone and the concentration of the reactants in this zone controlled by monitoring wells downstream from the ground water injection wells. Monitoring of the following parameters was carried out on a daily basis: controlled pH values, temperature, electro conductivity, dissolved oxygen concentration, redox potential, and chloride concentrations of Cr^{6+}.

By the results of study defined that ferrous sulphate with molasses or without it shown the best results of all the used reducing reagents. It is cost-effective reagent with fast and predictable reactions. By the end of geochemical study was made a decision on using ferrous sulphate ($FeSO_4 \cdot 7H2O$) for the treatment process.

Numerical modeling

The three-layer model developed was used to estimate transport processes of Cr (VI) and fine sediments in an alluvial stream. Model was created in Visual MODFLOW using an upstream weighted finite-difference method (VM Tutorial, 2014; VM User's Manual 2006) resulting in greater stability when simulating complex nonlinear systems (Hill M.C., 1992; Yang Q.C. et al, 2011). The description of the model preparation and calibration is described in Rykhluk T.N., et al, 2009 and Petrova A.P., et al., 2012. Figure 3 shows the results of model calibration on a period before treatment.

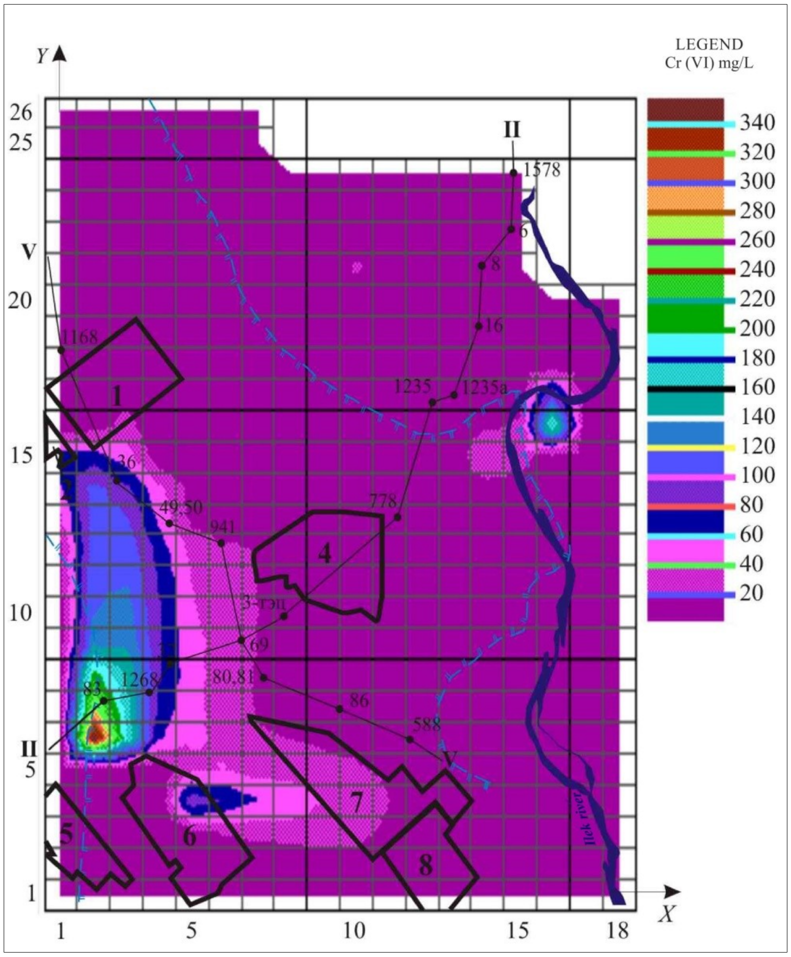

Figure 3. Area of groundwater contamination by the results of numerical modeling

Calibrated model helped to make reliable forecasts of groundwater pollution and transport in the industrial zone, estimate scope of work for the treatment operations, visualize, and manage treatment process (Salybekova V., et al., 2014)

Technology Description

Treatment technology is based on creating reactive zones by injecting reagents (an aqueous solution of ferrous sulphate ($FeSO_4$)) in predetermined locations within the contaminated groundwater plume and allowing them to "react" with the contaminants. Schematic treatment technology is shown in Figure 4. Groundwater is not extracted on this scheme. It is a passive treatment system.

By the results of groundwater modeling the treatment site was divided in three categories with high, relatively low and low concentration of chromium (Figure 5).

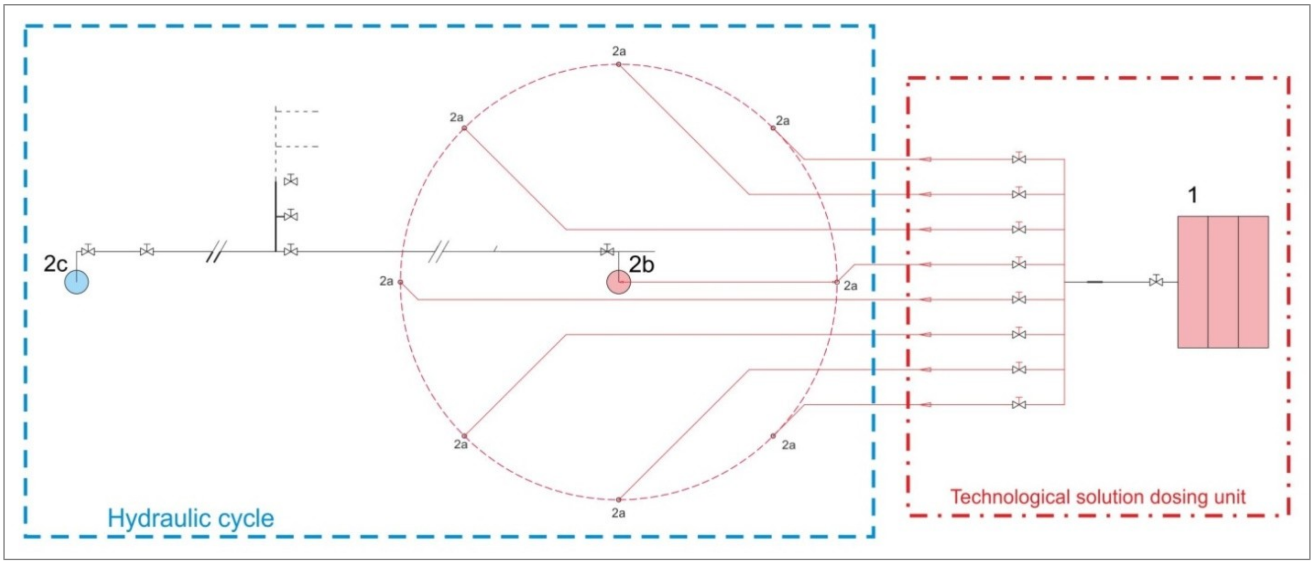

Figure 4. Groundwater treatment technology on a site.

Legend: 1 – technological solution (reagent) reservoir; 2 – injection site; 2a – injection blast hole; 2b – technological well; 2c- pumping well.

To form optimal reagent saturation of the aquifer all treatment operations were made in three phases by creating hydrocycle in the aquifer. To create hydrocycle wells on a site used for injection and pumping separately.

On Phase 1 (Figure 6) reagent injected in zones 1and 2 during the pumping from zone 3. Totally for the site used 13 injection wells, each with 8 blast holes and 5 wells for pumping.

Phase 2 illustrated on Figure 7. During this step injection to the zone 2 with a ferrous sulphate reagent conducted during the pumping from zones 1 and 3.

Phase 3. During final phase treated groundwater from zone 2 injected to the buffering zones 1 and 3 where it was necessary (Figure 8).

RESULTS AND DISCUSSION

During the period of treatment 1875 tons of ferrous sulphate injected to the aquifer. At the beginning of the project 392 injection wells and blusters drilled but the number increased to 426 during the process of treatment as it was adjusted by the results of numerical modeling. All phases of in situ treatment conducted for three mounts each. At the end of treatment process hexavalent chromium concentration reached 0.05 mg/L. During the treatment process conducted laboratory analysis on hexavalent chromium concentration. By the results of testing prepared maps of hexavalent chromium concentration on each phase reflected on Figure 9.

By the results of survey revealed following advantages of using in situ technology (U.S. EPA, 2000):

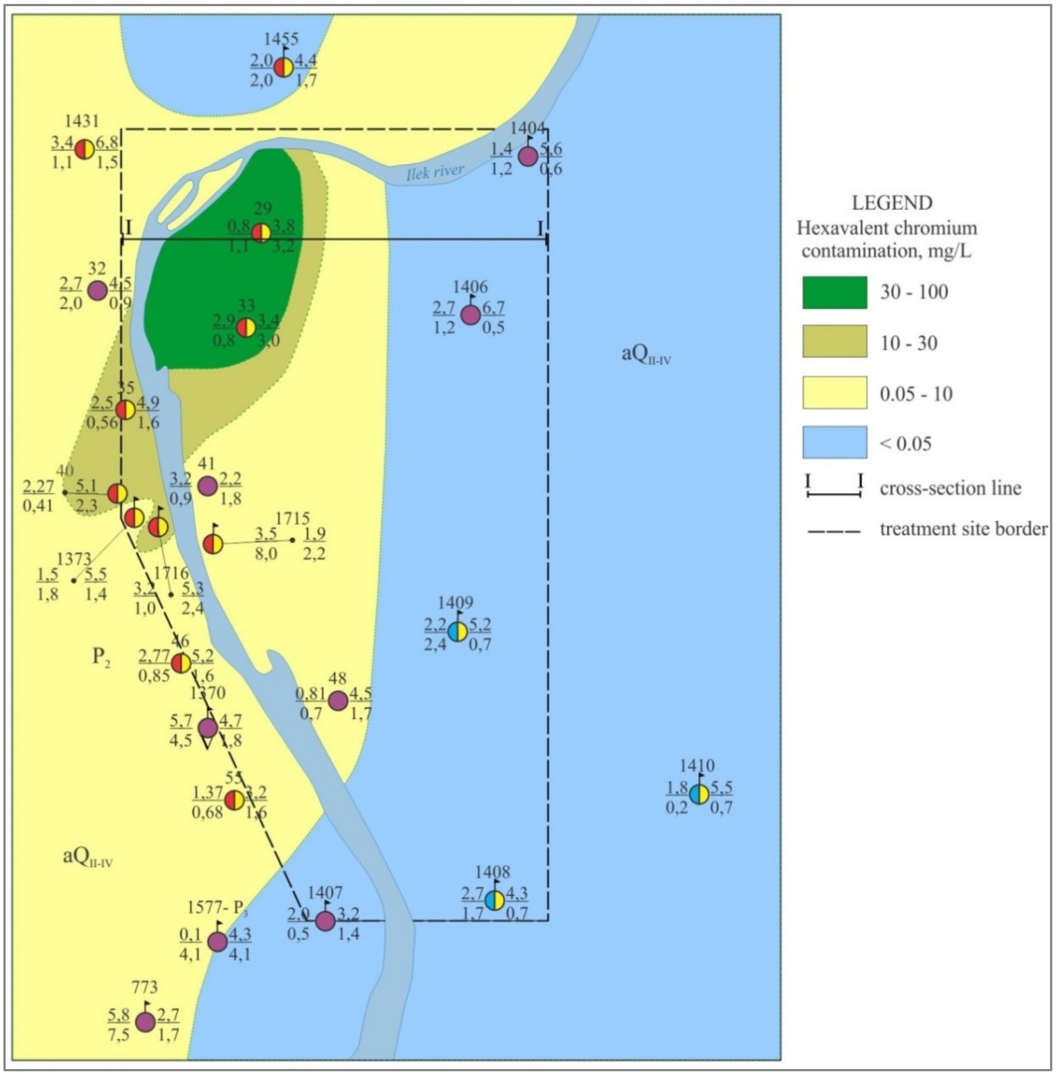

Figure 5. Groundwater contamination zoning

- Eliminates the infrastructure required for a pump-and-treat system; no disposal of water or waste. Inexpensive operation; reagents are injected at fairly low concentrations and the only sampling required is groundwater monitoring;

- In is possible to apply in situ on depth; no physical limits as with PRB;

At the same time there are some limits on using in situ method:

The metal is not actually removed from groundwater, it is only put into a relatively stable nontoxic state and will no longer interact with it;

May not remove source of contamination; mitigates contaminant plume;

Low permeability sites may preclude use of this method, but may be applicable to source zone treatment;

Despite ferrous sulphate shown good results on groundwater treatment it is still question of application biotic components for creating reactive zones.

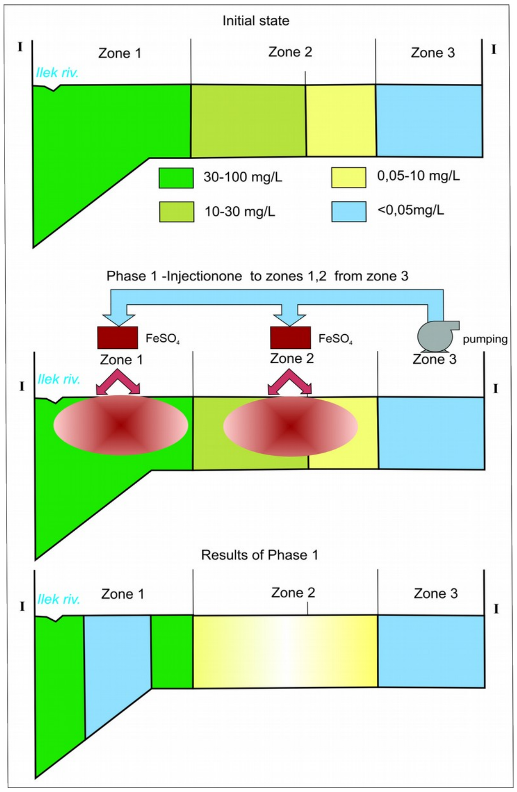

Figure 6. Treatment technology Phase 1

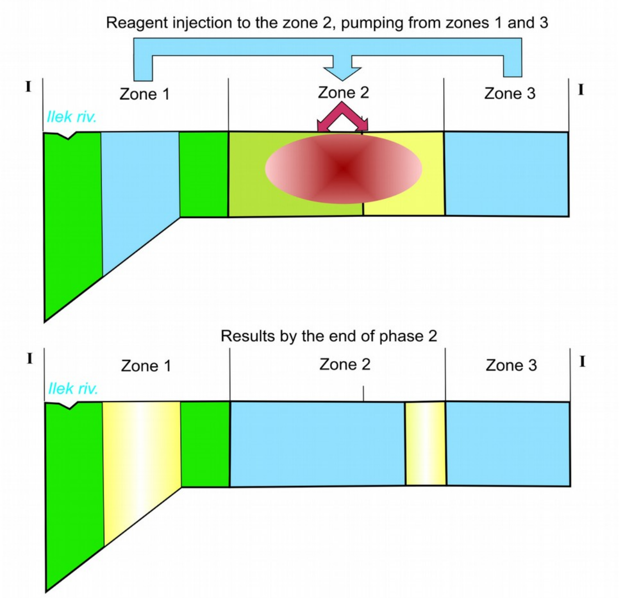

Figure 7. Treatment technology Phase 2

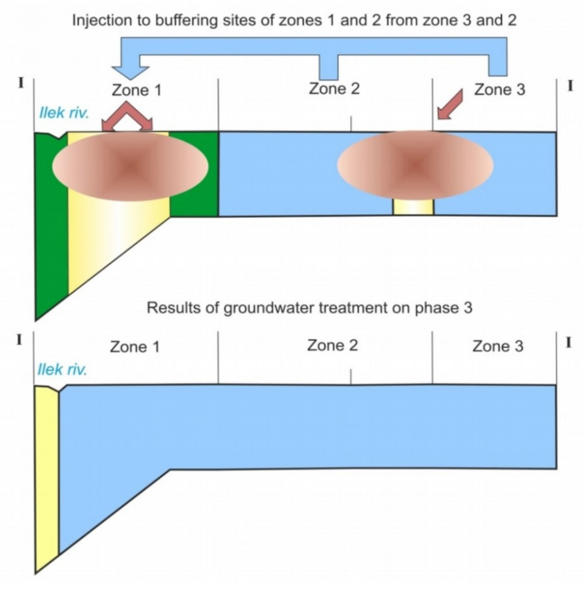

Figure 8. Treatment technology Phase 3

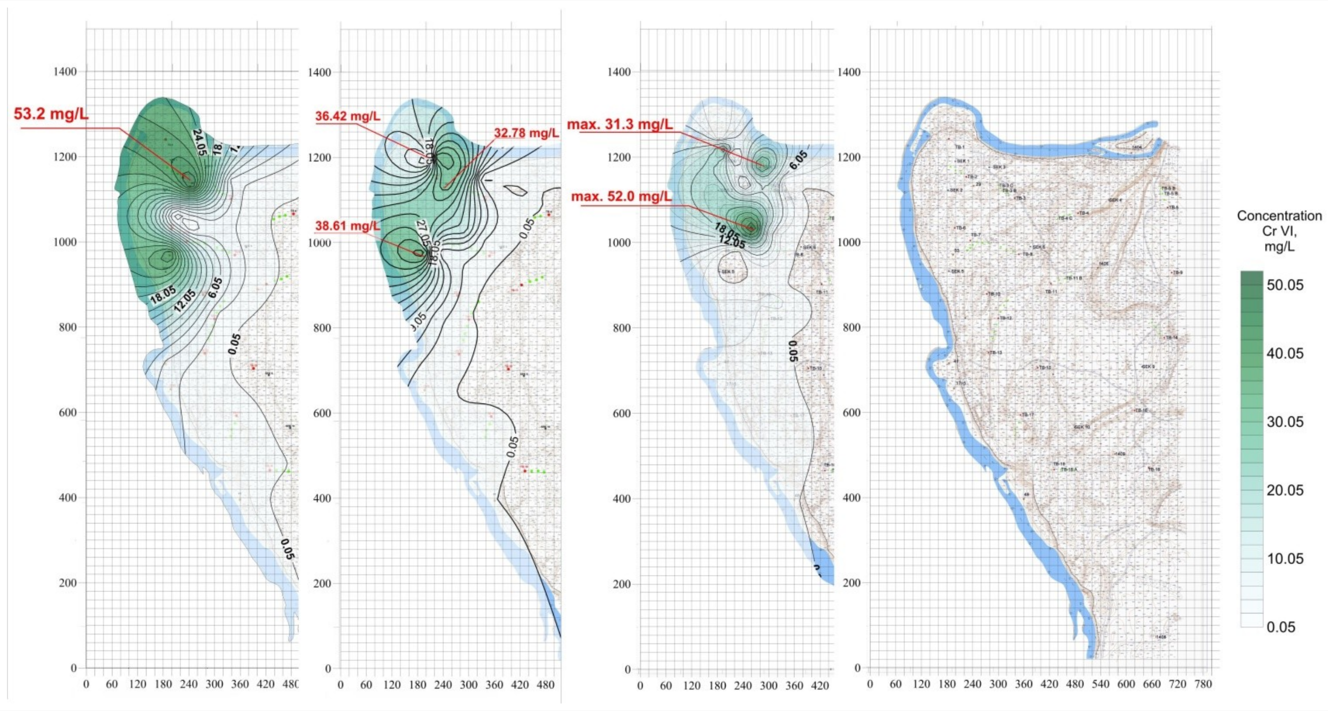

Figure 9. Concentration of Cr (VI) during the phases of in situ treatment

ACKNOWLEDGEMENTS

This paper was reviewed by Professor Amin Zollanvari, School of Engineering, Nazarbayev University, Kazakhstan, and Dr. S. V. Lubchyk , Universidade Nova de Lisboa, Portugal.

Publication and study grant funded by Ministry of Education and Science of the Republic of Kazakhstan. A special thanks to Dr. Burakov M.M. (LLP “KazHydek”, Kazakhstan) and PhD Tomas Saks (Latvian University, Latvia) for the support and valuable consultations.

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