EVALUATION OF DEMERCURIZATION EFFICIENCY OF CHLOR-ALKALI PRODUCTION IN PAVLODAR CITY, KAZAKHSTAN

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The case of mercury contamination in Pavlodar typical for the former USSR has resulted from chemical plant PO 'Khimprom" activity in 1975-1993 containing chlor-alkali production based on electrolysis with mercury cathode at the production capacity of 100000 tans of chlorine per year /1/. Due to the economic crisis in mid 1990s the chemical plant was in fact decommissioned and most of valuable facilities were utilized. Total load of metallic mercury got to the environment for less than 20 years and mainly deposited in soils was estimated to be 1310 tons. A plume of groundwater about 400 m wide polluted with $HgCl_2$ up to a concentration level of 0.1 mg/L has spread over basalt clay stratum at the depth of 5-20 m 2 km far from an electrolysis shop to the north-west (fig.1).

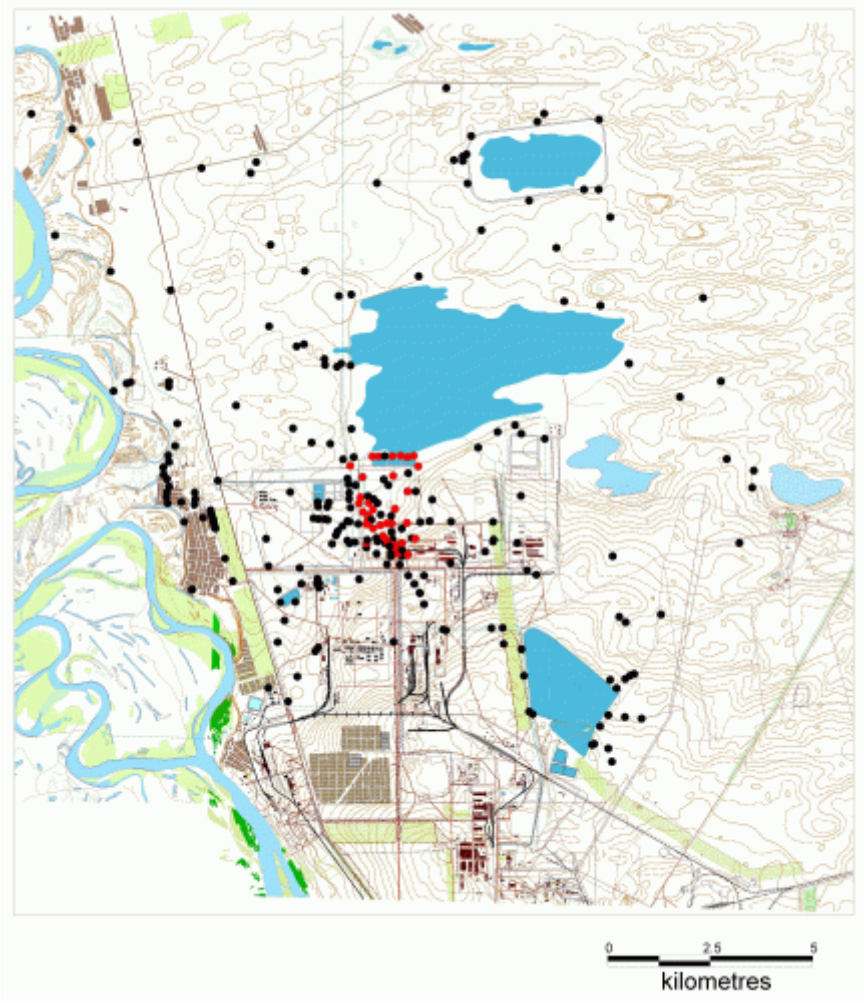

Figure 1. *The area of field works on the project ICA2-CN-2000-10209 "Toxicmanagement" in 2001-2001(dots on the map are groundwater sampling points; black ones – when mercury concentration in water is lower than 500 ng/L, red ones – higher than 500 ng/L)*

The plume was recharged with soluble mercury compounds from two sources: the major one – accumulation of metallic mercury, alkaline and chloride brines under the electrolysis factory (fig.2) and the additional one – accumulation of metallic mercury and sewage under the building of a wastewater pumping station located 900 m far from the electrolysis factory downstream the groundwater flow.

Figure 2. *Electrolysis factory after closing down chlor-alkali production in 1993*

Main risks to the environment were posed by mercury emissions to the atmosphere from mercury contaminated semi-destroyed industrial buildings and topsoil as well as by dissolving buried mercury in groundwater followed by spread of this contaminated groundwater towards the Irtysh River floodplain located at a distance of 5 km to the west from the chemical plant. Mercury vapors and mercury containing fish caught by fishermen from a wastewater storage pond (the technical water body with capacity of about 60 million m^3 located 2 km far to the north from the plant) posed a risk to health of still working personnel and population living in the vicinity. Groundwater mercury contamination also could reach water-supply wells of large village situated 4 km far from the chemical plant between the plant and the Irtysh River.

The first phase of demercurization was completed at the beginning of 2005. It involved demounting and utilization of all processing equipment of chlor-alkali production, manual collection of metallic mercury, dismantling of mercury contaminated production buildings, partial removal of heavily contaminated topsoil, and isolation of main underground hotspots of elemental mercury and mercury wastes from the atmosphere and groundwater, construction of a landfill for mercury containing building structures and the facility components. Some cleanup works had to be conducted in extreme conditions. So in spring of 1999 at the beginning of the works intensive evaporation of spilt metallic mercury occurred on dismantling the electrolysis building roof. All the territory the chemical plant owned was declared to be an emergency zone. The state of emergency lasted for two months until complete dismantling of the electrolysis hall and manual collection of most mercury spilt (17 tons).

According to original plan of demercurization (developed by JV “Evrohim”, Kien in 1995) it was prescribed to recover most metallic mercury occurring under the electrolysis factory (about

900 tons) by means of gravitational separation of pulp prepared of mercury contaminated soils as well as of thermal treatment of concrete debris of the factory floor slabs in a special furnace.

However monitoring research conducted in 2001-2002 on INCO Program of European Union found wider boundaries of contaminated area extent and hotspots unknown before that necessitated expanding substantially scope of remediation activity. That is why the proposal was accepted: to replace the strategy of mercury recovery by more cost-effective one of containment of main sources of mercury pollution. The containment strategy proceeded from understanding of impossibility of to achieve sanitary standards for mercury in all polluted media as well as absence of demand for commercial mercury at the legal market.

Figure 3. *Construction of anti-filtration barrier "cat-off wall" around electrolysis factory*

Four mercury heavily contaminated underground hotspots (under the electrolysis factory, a plant for mercury containing wastewater treatment and a wastewater pumping station as well as a repository of mercury wastes and sludge) were isolated along their perimeter from groundwater by constructing anti-filtration barrier so called "cut-off wall" at the depth down to 20 m 0.5 m deepening inside the basalt clay stratum. The cut-off wall 0.6 m thick was made of clays similar to bentonite and having filtration coefficient not more than 10^{-7} cm per second. The cut-off wall

was constructed using two unique excavators equipped with a clamshell scoop fixed on a vertical pole (fig.3). Total length of the cut-of wall was 3588 m. Concrete floor slabs remaining of chlor-alkali facilities were isolated fro the atmosphere with compacted clay cap and at the repository for mercury wastes and sludge – with multilayer cover (ash, gravel, fertile soil and turf). The landfill for mercury containing building structures and components of chlor-alkali facilities was located 50 m far from the electrolysis factory and represented a pit down to 3 m deep with compacted clay layer 0.5 m thick and filled up with different materials containing not more than 1% of mercury and soil-concrete solution. Having formed monolith it was covered with asphalt to prevent from dusting. The area of the asphalt shield has amounted to 15810 m^2 (fig.4).

Figure 4. *Landfill for mercury wastes at the territory of chlor-alkali production*

Post-demercurization monitoring was conducted in 2004-2007 within the framework of ISTC K-1240p project and involved observation over mercury concentrations in near-earth atmosphere, groundwater, and topsoil within the polluted area around the industrial site of chlor-alkali production as well as in bottom sediments, water and fish in the wastewater storage pond.

Measurement of mercury vapor concentration over insulating protective screens at the repository of mercury wastes and sludge as well as over the landfill for mercury bearing building structures gave values lower than 100 ng/m^3 that proved their reliable insulation from the atmosphere. However the clay screens covering concrete foundation of demolished buildings of chlor-alkali production turned out to be washed away by rainfall and flood flows in many places. In summer time concentration of mercury vapors was steadily above 10000 ng/m^3 over track of dried streamlets which were studded with visible drops of metallic mercury.

Measurements of total mercury content in water samples taken from observation boreholes network showed that despite insulation of underground mercury hotspots, general configuration of the groundwater contamination plume and level of dissolved mercury concentration on the whole were the same during three years of the monitoring. Significant local decrease in mercury concentration in the groundwater was found only at the territory of the chemical plant outside of the site of chlor-alkali production to the west of the former electrolysis factory; the reason of this could be slight deviation of the plum of contamination under flank action of new sources of

water loss from underground sewage system of the plant rather than cessation of the groundwater recharge with soluble mercury compounds from the main underground hotspot. It was shown that topsoil contamination with metallic mercury at the most of industrial area of the former chlor-alkali production was still abnormally high (up to 0.1% mass) and was a source of emission of high mercury concentration vapors to the atmosphere (above the level of 300 ng/m^3 in near-earth air layer 0.5 thick at 27^{o}C). The same topsoil could become the main source of groundwater recharge with soluble mercury compounds due to infiltration of atmospheric precipitation and water from melted snow through it that in general kept high level of mercury concentrations in the groundwater within the industrial site of chlor-alkali production. The plume of contamination also kept a tendency to transition of dissolved mercury of high concentrations in the direction of groundwater movement resulted in finding mercury in earlier uncontaminated observation boreholes of the monitoring network which monitored west direction of the mercury spread.

Soil sampling outside of the industrial area of the chemical plant allowed finding one more mercury hotspot at the area of a pasture inhabitants of nearby village used for their livestock. A level of the topsoil contamination was 100 mg/kg; the area of contaminated site was not less than 0.05 km^2; the place of contamination coincided with the area of the plum of groundwater mercury contamination spread at the depth of 6-8 m. Possible groundwater rise up to the ground surface as well as the topsoil mercury contamination resulted from the water evaporation was earlier predicted by simulation of the groundwater behavior using computer modeling software GMS 6.0.

Post-demercurization monitoring suggested a necessity to conduct the second phase of remediation works. Topsoil within the industrial site of the former chlor-alkali production contaminated with metallic mercury has still been the source of main risk so undoubtedly it must be treated using cost-effective technology. Also more reliable cap covering concrete foundation of the demolished buildings of chlor-alkali production must be constructed. Only then the correct investigation can be conducted to reveal the efficiency of the anti-filtration barrier – "cut-off wall" around underground mercury hotspots.

Because of the high potential dander posed by mercury contaminated groundwater a long-term seasonal monitoring of movement of the plum of mercury contamination including monitoring of mercury accumulation in topsoil in places of polluted groundwater rise up to ground surface must be arranged. In case of a real danger of the contamination occurrence in the vicinity of sources of population water supply either a technology of the polluted groundwater interception with help of drain wells or cost-effective technology of mercury immobilization within the plum of the contamination must be applied.

In /2/ literature containing additional information on this problem is given.

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