10th International Conference on Contamination Soil.
Proceedings of ISTC Science Workshop at the International Conference on Contamination Soil, Consoil 2008 (Milan, Italy 3-6 June 2008). ISTC, M., P. 104-106

Demercurization and post-demercurization monitoring in the area of an industrial site of a derelict clor-alkali facility in Pavlodar city, Northern kazakhstan

Mikhail Ilyushchenko, Paul Randall, Trevor Tanton, Rustam Kamberov, Lyudmila Yakovleva

The case of mercury pollution 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 tons of chlorine per year /1/. Due to the economical 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 an environment for less than 20 year and mainly deposited in soil 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 the basalt clay stratum at the depth of 5-20 m 2 km far from an electrolysis factory to the north-west. It was recharged with soluble mercury compounds from two sources: the major one – accumulation of metallic mercury, alkali and chloride brines under the electrolysis factory and the secondary one – accumulation of metallic mercury and sewage under the building of wastewater pumping station 900 m far from the electrolysis factory along the groundwater flow direction.

Main risks to environment were caused by mercury emission to atmosphere from mercury contaminated ruins and topsoil as well as mercury polluted groundwater possible spread to the Irtysh River floodplain located 5 km far to the west from the chemical plant. Risk to health of still working personnel and population living near the plant was posed by mercury vapors and mercury contaminated fish caught by fishermen from wastewater storage pond (technical water body with capacity about 60 million m^3 located 2 km far to the north from the plant). Groundwater 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 consisted of dismantling and utilization of all processing equipment of chlor-alkali production, manual collection of metallic mercury, demounting mercury contaminated production buildings, partial removal of heavily contaminated topsoil, and isolation of main underground hotspots of elemental mercury and mercury wastes from atmosphere and groundwater, construction of landfill for mercury-bearing building structures and the facility components. Some works were 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 after the roof of electrolysis factory had been destroyed. All territory the chemical plant owned was announced to be in a state of emergency, which lasted for two months until complete dismantling of the electrolysis hall and manual collection of most mercury spilt (17 tons).

According to original design of demercurization (developed by JV “Evrohim”, Kiev 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 efficient one of containment of the main sources of mercury pollution. The containment strategy proceeded from understanding of impossibility to achieve sanitary standards for mercury in all polluted media as well as absence of demand for commercial mercury at the legal market.

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 at 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 depths down to 20 m with 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. Total length of the cut-off wall was 3588 m. Concrete floor slabs remaining of chlor-alkali facilities were isolated from an atmosphere with a compacked clay cap and at the repository for mercury wastes and sludge – with multilayer cover (ash, gravel, fertile soil and turf). The landfill for mercury bearing 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 lined 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 monolyth it was covered with asfalt to prevent from dusting. The area of the asfalt shield has amounted to 15810 m^2.

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.

Measurements of mercury vapors concentrations 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 atmosphere. However the clay screens covering concrete foundaton of demolished buildings of clor-alkali production turned out to be washed away by rainfall and flood flows in many places. In summer time concentration of mercury vapors was stably above 10000 ng/m^3 over tracks of dried streamlets which were studden with visible drops of metalic 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 plum 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 atmosphere (above the level of 300 ng/m^3 in near-earth air layer 0.5 m 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 flood flows 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.

In 2002 a regional hydro-geological model of the Northern industrial area of Pavlodar was produced with help of a system of computer simulation GMS 3.1, database formed on the basis of data collected on the special monitoring network from more than 100 observation boreholes for two years as well as historical data on the industrial area including description of more than 2000 boreholes constructed here for 40 years. In 2007 the model was converted to GMS 6.0 software format and improved by a local model of the groundwater mercury contaminated area as well as data of monitoring of 2004-2006. The regional model allowed explaining mechanism of formation of the plum of groundwater mercury contamination, gave possible scenarios of its development and predicted groundwater rise up to the ground surface at some places and topsoil mercury contamication caused by the groundwater evaporation. It was shown that even at complete cessation of groundwater recharge from both underground hotspots and topsoil the plume of groundwater mercury contamination would still exist for more than 30 years slowly shrinking and bringing mercury concentration levels down due to dilution and sorption processes. Since dynamic of groundwater spread in this region is determined in general by man-caused factors, the direction of the plum of contamination development can be changed quite quickly. Change in direction of groundwater mercury contamination spread to the wast to the Irtysh River and a large village in the vicinity can become one of results of nowaday reconstruction of industry at the Northern industrial area of Pavlodar caused by modernization of economics of Kazakhstan.

Monitoring of seasonal variations of water-level of the wastewater storage pond constructed at the place of two small natural salt-water lakes which had had maximal depth of 10 m has shown that its water-level has been close to its maximal fillup yet even in the absence of wastewater discharge there for already 15 years. This resulted from underground recharge of the pond provided by a joint ash lagoon (located 5 km to the south) of two large heat power plants. After wastewater discharge cessation surface waters of the wastewater storage pond have self-purified substantially (at present total mercury content there is about 0.0001 mg/L) and colonized with fish mainly silver crucian. About 2.6 km^2 of its shoreline is covered with reed thickets while total water-surface area is 17.8 km^2. Usually in summer time bottom sediment sampling is very difficult to do because of permanent roughness of water surface that is why it was conducted in winter time from under the ice up to 1 m thick covering the pond for 5 months per year. Technogenic silts were found to be accumulated only in a few depressions resulting in formation of deposits up to 1.75 m thick at the area of 5.9 km^2. Mercury concentration in the silts reached 1 g per kg of dry weight and amount of mercury there was estimated to be about 130 tons. Mercury concentration in fish reached its maximal value of 2.5 mg/kg.

Post-demercurization monitoring suggested a necessity to continue remediation works. Topsoil within the industrial site of a 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 foundations of the demounted buildings of chlor-alkali production must be constructed. Only then the correct investigation can be conducted to reveal efficiency of the anti-filtration barrier - “cut-off wall” around underground mercury hotspots.

At present the wastewater storage pond does not pose serious risk being a technical water body. However giving publicity to local population about a danger of eating fish caught in this water body must be a priority of local authority and mass media. Further fate of the wastewater storage pond depends on plans how to use it: in case of making decision to use it as a source of cheep technical water its contaminated bottom sediments can be removed or isolated cost effectively with help of a protective screen.

Because of the high potential danger 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 the technology of the polluted groundwater interception with help of drain wells or mercury immobilization within the plum of the contamination must be applied.

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

Acknowledgement

The work was funded by International Science and Technology Centre (www.istc.ru) in frame of the Project Development Grant K-1240p.

References

1. Mercury pollution at Pavlodar. http://Hg-Pavlodar.narod.ru
2. Mercury pollution management in Kazakhstan. http://Hg-Kazakhstan.narod.ru