Problems of management and efficient use of the Irtish River basin water resources.
The proceedings of International Scientific-Practical Conference (Omsk, May 20-21 2004).
Omsk, Publishing house "Nauka", 2004, P. 107-110. (Ru)

Demercurization of the mercury contaminated hearth at the area of the former plant "Khimprom" in Pavlodar

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Pavlodar "Khimprom" plant produced chlorine and caustic soda by means of electrolyses with mercury as a cathode since 1975 till 1993. Totally the Building 31 contained 80 electrolyses cells CDM 150-7.3 (in 1975 – 72 pieces, in 1984 – 72 + 8, and after major repair in 1986, – 68 cells). Industrial year output of the plant was equal to 112 700 tons of caustic soda and 100 000 tons of chlorine. The design load of metallic mercury for one cell amounted 2400 kg, while the scheduled load was - 2750 kg. Operating temperature of solutions - 75-100^{0}C.

Based on the data /1/ 685 525 tons of caustic soda were produced and 1089,356 tons of mercury were utilized* since 1975 till 1989 for 14 years of the plant operation. This amount came to the specific mercury consumption equal to 1,589 kg/t, whilst "scientifically proved consumption" regulated the level of it as 0,3 kg/t, "technically proved consumption" – 0,5 kg/t and "planned consumption" – 0,76 kg/t. Mercury technological loss balance was reported as follows: less 1% - slime, accumulated and treated at the site, up to 2% - emission from ventilation, up to 3% - slime to be treated at mercury refinery, up to 4% - losses from emission along with hydrogen, up to 12% - desalinated slime, to be transported to the settling ponds of solid and liquid wastes, up to 80% - unaccounted losses. The latter were stipulated for spills and leakage of metallic mercury and failure to collect the whole spilt amount in the course of both operation process and cells repair. The biggest loss of mercury was reported at the time of the plant closing and the subsequent equipment dismantling in the late 1990s.

In 1988 in the Soviet Union the Program of the electrolyses plants technology shift into membrane type was passed, and since 1990 the practical development of membrane technology in chlorine industry is reported to start (that was a time of new electrolyses Building construction nearby Building N 34 in the Pavlodar "Khimprom" plant). However due to the collapse of the USSR this work was completely stopped. Inadequate technical repair of the chlorine production triggered the Resolution of the USSR chief sanitary doctor

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* This data allows to approximately evaluate mercury consumption as of 1310 tons for the whole period of chlorine and caustic soda production in the Pavlodar "Khimprom" plant, 300 tons of which were returned as a commodity mercury. According to the data /2/ the plant mercury consumption in late 80s and early 90s was estimated as of 120 tons per year, which results in total mercury consumption of 2000 tons for 18 years.

№ 89-35 of 12.07.89 "On interdiction of chlorine and caustic soda production at the Pavlodar plant "Khimprom". Nevertheless, for the more several years the manufacturing process went on with interruption. Electrolyses shop was stopped completely in August 1993 and in January 1994 Kazakhstan Cabinet of Ministers issued the Resolution № 7 "On measures for rehabilitation of environmental and sanitary situation in the Pavlodar industrial area (Pavlodar plant "Khimprom")" which didn't leave behind any hope for the plant rehabilitation, as it gave the freedom for "sale of disengaged both equipment and materials of no use in the plant". Dismantling of the expensive equipment and non-ferrous metals was put into practice in 1994-1995.

In 1989 Kiev scientific and research division of GOSNIICHLORPROJECT (since 1993 - it is JV "Eurochim") was assigned to study mercury contamination level in the plants "Caustic" in Sterlitamak and "Khimprom" in Pavlodar and to obtain the materials for a design of demercurization of the inactive equipment and contaminated wastes burial. In Pavlodar this work was carried out in 1989-1992 together with Pavlodar hydrogeological expedition "Technolog" and in 1995 was resulted in the draft project "Demercurization of inactive caustic soda and chlorine production". The project foresaw the dismantling of the Building 31 and storing the low contaminated constructions in a burial ground intended for the demercurized wastes, and which is 70 meters southward the Building 31. The burial ground was supposed to be a pit less the 3 meters deep, the bottom of which was covered anti-filtration clay screen of thickness 0,5 meters. Other wastes with low mercury content after its treatment in the burial ground with cementing agent were supposed to become a monolith, capable to prevent mercury leaching. The concrete floor in the Building 31 after its removal had to be crushed to the size 200-300 mm and those floor pieces, which mercury content was higher 0,3-0,5%, to be sent in containers for the thermal demercurization. The thermal demercurisation had to be carried out in a chamber of an electric oven with recurring action and air cooling condensation and adsorption, loaded with activated charcoal AG-3, impregnated with ferrous chloride.

It was supposed to heat the mercury-contaminated materials during two hours to the temperature of 700-750^{o}C. Concrete crushed pieces thermally treated, as well as those ones with low mercury content had to be buried either. Ground and soil of 2,5 meters deep under the Building 31 with concentration of mercury content less then 1 % were to be extracted. These ground and soil were planned to undergo the mechanic break-off in the trommel scrubber, where the ground pieces had to be decomposed, washed and screened. From obtained pulp the mercury was supposed to be recovered by settling, then the pulp had to be partially dried and used for soil-concrete additives. For this purpose it was planned to use grounds with low mercury content either from the ground layer 0-25 cm at three sites near the Buildings 31, 31A, and 37. The sites after the ground extraction were to be restored by filling with clean ground. The soil-concrete ground was assumed to be prepared in a concrete blender with portland cement – 400 and be stored in demercurized wastes stock as a cementing agent. To prevent spreading of mercury in ground water under the Building 31 – that is an epicenter – the cutoff wall of up to 20 meters deep was stipulated for a construction as an anti-filtration screen around the Building 31. The anti-filtration screen had to be constructed by "wall in ground" method, the bottom of which would reach water-resistant basalt clay under aquifer.

For some years, the Project was a subject to expertise and discussion in the oblast and state bureaucratic institutions having practically no hope for its funding initiating. In 1998 the support for the Project provided by Mr. D. Akhmetov - the oblast akim (governor) - and small funding at the account of the oblast budget became a crucial point. These financial resources only were enough for the roof removal of the Building 31 that led to intensive mercury

vaporization in summer of 1999. The Pavlodar city akim declared the state of emergency in the city and, the same year under the pressure of public and mass media, the Government of the Republic of Kazakhstan allocated the funds for both the dismantling the main part of the Building 31 and spilt mercury collection. After the funding was spent the scheduled activity was halted. The Government of France offered the financial and technical support in demercurization activity. This offer was accepted by the RK President N.Nazarbayev and the French state company BRGM was assigned to study this problem and carry on an appropriate negotiation. The French specialists proposed as a first stage of their project, which was estimated of 8 millions USD provided as a state loan, to study the mercury contamination status at the area of the site "Khimprom" which is similar to "Eurochim" study and "hot tests" of technology of thermal mercury abstraction from the contaminated grounds and construction wastes in the special pilot plant. Kazakhstan party insisted on the urgent implementation of the Demercurization Project on the base of "Eurochim" version without being changed otherwise it would prolong the state of emergency. Those negotiation lasted till 2001 and fruitless came to the end.

In the framework of EU Program INCO-2 in 2001 Consortium of seven Kazakhstani and foreign universities, research institutes and companies started the implementation of two-years investigation project "Toxicmanagement", aimed at the risks assessment of mercury contaminated soils and ground water in the north outskirts of Pavlodar in the area of "Khimprom". The very first recommendations, put forward by the researches of "Toxicmanagement" just after some month of the project implementation, proposed urgent continuation of dismantling the Building 31 and other buildings of chlor-alkali production, which were contaminated with metallic mercury and were the source of intensive mercury emission into the air. In 2002 state budget funding of the Demercurization Program was recommenced and the project was carried out along with "Toxicmanagement", and that allowed to make timely necessary amendments in it. Participation of Kiev "Eurochim" specialists precipitated the final adjustment of the Demercurization Project. The adjustment has been finished by the end of 2003. The completion of the demercurization work at the Site N 1 of the former Pavlodar plant "Khimprom" as well as at the area between Site N 1 and waster water settler – lake Balkyldak was scheduled for the end of 2004. "Toxicmanagement" study reported that the hearth of mercury soil and ground water contamination in the western part of the Site 1 that included besides the Building 1 other buildings of chlorine-alkali production, is not the only source for the risk posed for environment and population in the reported area.

The same rate of danger is represented by the effluents and solid wastes ponds and contaminated with mercury soils nearby as well as mercury bearing sediments in the settler – lake Balkyldak. Furthermore, mercury contaminated ground water plume moves from the Building 31 towards north - north-west and it has already reached 2,5 km in depth of 6-14 meters below basalt clays of Pavlodar assise. It was also reported, that the cause of mercury plume appearance was metallic mercury deposited under the Building 31 as well as the secondary mercury hearth located at the waste water pump station N 6.

Obtained in the course of implementation "Toxicmanagement" results were openly discussed, including in the Presidium of Kazakhstani Academy of Science /3/, and this allowed to come to agreement on the necessity of adjustment of the original "Eurochim" Project version. It was decided to store in sarcophagus only those construction materials of the chlor-alkali production buildings (Buildings №№ 31, 31A, 34, 34A) whose mercury contamination was not more then 0,3%. Mercury abstraction from under the electrolyses shop in Building 31 and abstraction of grounds located under its floor were delayed for the uncertain future because the applied technology of the "wall in ground" construction is fail-safe for isolation of the deposited mercury from ground water.

Besides, at present the metallic mercury as it is does not represent any commodity value but requires special measures and spending for the safe storage /4/. It was also proposed to enlarge the area being isolated with anti-filtration screen by the “wall in ground” by means of inclusion the area of the Site 1 around the buildings 31A, 40, 40A, 40B and around the pump station N 6 and waste storage ponds into isolated area. The upper layer of soils contaminated with mercury over 10 mg/kg, should be abstracted from the depth of 50 cm and be placed inside the perimeter which is protected by the screen (mainly at the area of the waste storage ponds). Afterwards these sites should be restored with clean ground. It was also proposed to cover the materials isolated with “wall in ground” around the Building 31 and waste storage ponds so that they are sealed and protected from the mercury vaporization and rainfalls penetration. It will require the construction of the special coverage, which will simultaneously prevent gas mercury emission as well as the capillary rise of metallic mercury and contaminated ground water.

The work completed by the present time absolutely excludes the risk of gas mercury contamination in the residential area of Pavlodar and the thread of contamination of the river Irtysh. To monitor the level of risk, posed by the remaining mercury pollution, the network of observation bore-holes (more then 100 in sum) was set and the Program of post-containment management and monitoring of mercury pollution in Site of Former PO “Khimprom” was developed. This program is scheduled till 2020.

References:

1. E.N. Lushin. Report on mercury contamination study at the site of caustic soda and chlorine production in Pavlodar Chemical Plant. V 1. NTC "Tekhnolog", Pavlodar, 1990, 41 p.
2. Mercury in environment of Siberia: assessment of natural and anthropogenic contribution. Novosibirsk, 1995, 30 p.
3. T.W.Tanton, V.V.Veselov, M.A.Illyushchenko, V.Yu. Panichkin. Assessment of risk posed by the mercury contamination in the northern industrial zone of Pavlodar city. Kazakhstani Academy of Science reports. №4 (2003), P.78-81.
4. P.Randall, L.Brown, L.Deschaine, J.Dimarzio, G.Kaiser, J.Vierow. Application of the analytic hierarchy process to compare alternatives for the long-term management of surplus mercury. J. Environmental Management, **71**, (2004), P.35-43.