Promyshlennost Kazakhstana.
№ 3 (6), 2000, P. 56-59. (Ru)

The mercury pollution of the Nura River

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The mercury contamination of the Nura River /1-5/ has been begun since August, 1950, when the Karaganda Factory of Synthetic Rubber (SR) (since 1982 - PO «Carbide», from the beginning of 1990s - joint-stock company (AO) «Carbide») sets to development of production of acetaldehyde on the Kucherov method by a direct hydration of acetylene at the presence of the catalyzer - sulfate salt of mercury (II) in Temirtau city. Project development was carried out by «Hiprokauchuk" of Moscow City. The technological schema of acting acetaldehyde production of the firm IGFarbenindustry of Osventsim City, and also equipment which had been removed from Germany on reparations after ending of World War II were used.

The Kucherov reaction was implemented in hydrators (three hydrators were used from 1950 to 1964, four - from 1964 to 1995, three - since 1995). Hydrator is a hollow column by height of 17 m with the upper expanded part, filled with reaction solution (contact acid):

$H_2SO_4 + Fe_2(SO4)_3 + HgSO_4$. Acetylene and steam were forced into lower, conical part of the hydrator. The acetylene bubbling through the contact acid, was transformed to acetaldehyde on 60 %, the vapors of which one came out of the head of the hydrator together with unreacted acetylene, steam and mercury vapors. The mercury vapors were generated as result of blowing-off of atomic mercury at the moment of reducing of Hg (II) by impurity gases of acetylene. The impurity atomic-dispersed elementary mercury was present in whole further technological chain (separation of acetaldehyde from unreacted acetylene, concentration of acetaldehyde and its transformation to an acetic acid and ethyl acetate, the regeneration of acetylene) polluting both the products of the manufacture* (acetaldehyde, acetic acid, ethyl acetate) and the waste products (wastewater and distillation residue). Ventilation releases of the hydration shop, the acetic acid and ethyl acetate productions contained the mercury vapors. The mercury vapors were also formed under chilling of the

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* The aqueous acetaldehyde, before to be subjected to rectification, previously passed through coke filter to be clearing from mercury, however level of this clearing was low.
Regeneration of the contact acid was carried out at the cost of adding of a metal mercury, which was oxidized by Fe (III) to Hg (II) in hydrator, and also at the cost of settling, blowing-off of organic compounds by a direct steam and oxidizing of Fe (II) to Fe (III) by concentrated nitric acid with subsequent stripping of the nitric oxides outside of the hydrator.

mercury polluted recirculated waters, in particular, distillation residue. The mechanism of Kucherov reaction expects creation of intermediate "quasicomplex" compounds of the mercury ions with molecules of acetylene containing a covalent linkage C - Hg. The mercury organic compounds with little molecular weight which are well soluble in water and distilling without disintegration were accumulated as a result of a side reaction in the hydrator. The part of them evaporated together with acetaldehyde and got into the further technological chain, another part was evacuated from hydrator together with a waste contact acid.

Waste materials of a contact acid - mercury sludge containing a settling of organic materials, the mercury salts and metal mercury, were treated by dry distillation, and since 01.01.76 had been sent to Nikitovski Mercury Combine. The mercury losses under a regeneration of the contact acid were both as a spillage of metal mercury, and as solutions containing dissoluble mercury salts, and also due to the mercury vaporization in process of treatment by direct steam. The mercury vapors were partially picked up by water in a mixture condenser and entered to sewerage as atomic-dispersed and compact metal mercury, and also were partially thrown out with ventilation releases.

The thermal recovery plant for mercury sludge* represent the mercury stove with fire heating and two water condensers. Oxide of carbon (II) or mazut was used as a fuel. 5-10 % of dry lime was added to mercury sludge to neutralize the acid. After stirring the obtained mass was by hand loaded into stove by portions 250-300 kg each. Temperature of sludge heating was 800-900^{o}C, duration of heating was 9-11 hours. Unloading of calcines from stove was carried out after 2-3 operations of furnacing. After the stove the mercury vapors together with flue gases passed through a number of mixture condensers, in which they were chilled by water refluxing. Mercury condensate together with water went to the collectors, periodically it was poured out of collectors into balloons. Surplus of water went into the drains. Underpressure inside of plant (20 millimeter of mercury) was maintained with the help of the ventilator, which drew the flue gases and ejected them to an atmosphere through an exhaust tube. The mercury losses in the process of dry distillation of sludge were as mercury vapors in composition of flue gases entering to an atmosphere, the calcines of mercury sludge which were removed onto a dump, the mechanical losses of mercury sludge on industrial site under their both transportation and loading into the stove and atomic-dispersed mercury taken out by cooling water from condensers to canalization.

Thus, the technological schema of acetaldehyde obtaining guessed the mercury losses as atomic-dispersed mercury and organo-mercury compounds in marketable products, metallic compact mercury, atomic-dispersed mercury, ion inorganic mercury and organo-mercury compounds in wastewater and gaseous mercury in ventilation releases.

Primary designed capacity of the production was 43200 tons of acetaldehyde per a year. Production was expanded up to 65000 t/year by 1964, and up to 76500 t/year by 1975. In 1995 the shop capacity was reduced down to 36000 t/year by reason of a removal of the second system of hydration from exploitation owing to a total decrease of the acetaldehyde demand and the equipment wear. In 1997 production of acetaldehyde was completely ceased. And in 1998 joint-stock company «Carbide» in Temirtau City was divided into three independent plants, the main of which including

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* Waste products of the contact acid regeneration (80 % of all treating waste materials), and mercury sludge from other mercury shops, and waste coke filters of a technological area of acetaldehyde purification were treated.

acetaldehyde production, was declared the bankrupt. There was demounting and sale of the equipment having though some value (mainly as metal scrap). However demercurization of manufacturing facilities of acetaldehyde production, treatment facilities, sewerage networks and territory of industry site can not be carried out by the plant, because there is a great technical and economical problem in view of their large-scale mercury pollution due to a long-term exploitation, absence of the demercurization project and resource.

First stage of treatment facilities of the Karaganda Factory of SR were gone into operation in December, 1950, second stage - in 1954. Feasibility study of the project was developed by Research Institute "Vodgeo" using the results of laboratory experiments of a similar plant in Shkopau City (Germany). The design was carried out by the Leningrad Department of Research Institute "Vodokanalproekt". Research Institute "Vodgeo" carried out the supervision over the construction and starting-up and setup operations.

Primary capacity of treatment facilities was 3000 м^3/day, after 1954 total capacity of the first and second stages of treatment facilities was 5500 м^3/day. The base element of the purification scheme of the first and second stages was the biological filter. It represents filter beds by depth 1,5 m arranged horizontally, germinating by bios of microorganism zoogel during maturing (for 1,5-2 months), and showered periodically from above out of atomizers with previously desilted waste water. The first stage of biofilters represented two sections 60 m × 33 m each. Half meter coke bed and below the meter bed of broken granite stone have been used as a filling agent. The second stage also represented two sections of filters of the same sizes, filled by crushed rock. All four sections were arranged in a not heated building, the foundation of which one was a receiving tank.

After purification on bio filters the sewage went into treatment tanks, where they were chlorinated and freed from silt taken out of bio filters. The clarified sewage went into Main Drain through underground collecting channel, and then into the Nura River. Tank silt accumulated in the treatment tanks, were moved onto sludge beds by size of 10 m × 25 m each to dry. In 1950 during first stage starting four sludge beds were gone into operation.

During starting-up and engineering setup operations the temporary filtration land plots - biological ponds were arranged on the Factory of SR. There was release of wastewater from temporary filtration land plots to Main Drain. In further the bioponds also accepted sewage of the Factory of SR during suspensions of treatment facilities, and also when there were substandard sewage (acidic, with pH lower than 6,0 or alkaline, with pH higher 9,0). Until 1969 (maybe even later) after liquidation of temporary filtration land plots the substandard sewage were discharged to the undrained swamp Zhaur.

At the beginning of 1960s in connection with the extension of carbide and acetaldehyde productions the construction of additional treatment facilities was started under the design of the Leningrad Department of Research Institute "Vodokanalproekt", which one was finished in 1966. The throughput capacity of the additional treatment facilities was 43000 м^3/day.

Seven aerotanks with capacity 4180 м^3 (4 - for first stage in 1961 and 3 - for second stage in 1966) were constructed and gone into operation. Additional treatment tanks, old sludge beds were restructured in 10 sludge beds by size of 100 m × 15 m each (1963) and 14 new sludge beds by size of 120 m × 18 m (7 - in 1964 and 7 - 1966) were constructed. The "Old ash lagoon" of KarGRES-1 have been stated to use as additional sludge bed and for deposition of fermented silts. Methane-tanks (2 - by capacity of 680 м^3 in the first stage in 1964 and 2 - by capacity of 1000 м^3 in the second stage in 1966) were constructed for anaerobic treatment of sediments.

In 1969 filtration land plots were constructed under the design of a construction department of the Factory of SR providing for an equalization about 1 million м^3 of substandard sewage per a year and their subsequent treatment on the treatment facilities.

The design documentation of the treatment facilities of 1950-1954, and also additional treatment facilities of 1961-1966 didn't provide for purification of sewage from mercury. The technological regulations of 1973 even recommended to use fermented silt after methane-tanks as fertilizer in an agriculture. However high mercury concentrations in wastewater of the Factory of SK not only exceeded sanitary norms, but also were a reason of a poisoning of the activated silt by mercury, that essentially made the operation of treatment facilities worse.

Since October 1973 and during 1974 the distillation residue of the plant of acetaldehyde rectification with mercury concentration 1,5-3 mg/l and volume 120 $м^3$/hour was mixed with sludge waters of the carbide production by volume of 300 $м^3$/hour and was directed to the sludge lagoon. After neutralizing by lime a generated wastewater by volume 420 $м^3$/hour with the mercury contents 0,04 mg/l were discharged through Main Drain into the River Nura.

In 1975 it was made a decision on urgent creation of local treatment plant for wastewater purification from mercury in territory of the Factory of SR. All mercury content waters including the distillation residue had to go through this treatment unite. The reduced model of purification of mercury content wastewater on Nikitivski Mercury Combine was chosen as the technological schema of local purification. Besides the problem of the mercury wastewater was supposed to be radically solved at the cost of shutdown of the production with the mercury catalyst and construction a new acetaldehyde production by a vapor-phase method on the basis of the cadmium catalyst by the end of the 1970s. A new acetaldehyde production has been constructing for several years, however, it was not finished because of the prohibition of Ministry of Health Services of KazSSR.

The local treatment plant for wastewater purification from mercury started its work in 1977. The schema of the purification included neutralization of wastewater by alkali NaOH up to pH 9.4 - 9.9, magnetic and sulfide treatment in a special treatment tank adding a polymer coagulant PAA and a solution of iron (II) sulfate. The plant capacity was 180 $м^3$/hour, degree of purification of wastewater from mercury was provided from a concentration level 3-10 mg/l up to 0,7-1,0 mg/l. Unlike Nikitovski Mercury Combine the acetaldehyde production wastewater contained a plenty of organic reductants, and also atomic-dispersed mercury. Therefore ion inorganic mercury here, mainly, was as Hg (I). An effect of sulfide-ions resulted in to formation of a mixture of sulfide of mercury (II) and dispersed metal mercury:

$Hg_2^{2+} + S^{2-} \rightarrow HgS\downarrow + Hg.$

Besides the wastewater of mercury shops contained plenty of indissoluble compounds of mercury and elementary mercury which were in suspended and colloid state. They also were not deposited completely in the process of sulfide treatment. Thus, sulfide purification without preliminary final oxidation Hg (I) and Hg (0) purified wastewater only from the compact metal mercury and some part of the ion inorganic mercury, transforming the another part to an atomic-dispersed state and thereby increasing its contents in wastewater. The organo-mercury compounds were not disintegrated by sulfide-ions and were not held by treatment facilities.

After local sulfide treatment the mercury content wastewater further went to a total canalization of the manufacture and onto the treatment facilities of the Factory of SR. At the cost of dilution up to volume 800-1000 $м^3$/hour the concentration of mercury in wastewater was reduced in ten times, and the concentration of mercury was once more reduced in ten times at the cost of microbiological purification. Wastewater of the Factory of SR with the mercury contents 0,01-0,02 mg/l were mixed with wastewater of "Karmetkombinat" and total sewage of Temirtau City in Main Drain. The average water flow in Main Drain was 5000-7000 $м^3$/hour. Mercury content wastewater of the Factory of SR, thus, were again diluted into

10 times, and the mercury contents was reduced down to 0,001-0,002 mg/l, that, nevertheless, was higher then maximum permissible concentration (0,0005 mg/l) in 2-4 times.

Mercury sludge formed under purification of wastewater on local treatment plant and containing up to 20 %mercury was sent in container for treatment onto Nikitivski mercury combine.

In 1980 the treatment facilities of the Karaganda factory of SR were reconstructed. The branch of bio filters was closed and equipment was demounted, however working area, broken stone and coke of biofolter were abandoned without demercurization. Methane-tanks were retools: two of them were begun to use as aerobic stabilization pond, another two - as degelminizator. The capacity of treatment facilities was reduced down to 43000 $м^3$/day.

Thus, in 1950s the mercury entered to the River Nura at the cost of discharge of the unpurified or partially purified wastewater (treated only on temporary filtration land plots or bio filters). From a beginning of 1960s the waste silts have been accumulating on the territory of the Factory of SR. About 10 tons of mercury per year has begun to go onto sludge beds together with these silts. This fact testifies about sharp reduction of contents of the mercury entering into the River Nura through Main Drain after the additional treatment facilities are gone into operation. However during all period of the Factory of SR existence waste sludge were deposited in «Old ash lagoon» of KarGRES-1, situated on a bank of the River Nura. However during all time of the Factory of SR existence the waste silts were deposited not only on the sludge beds on the territory of the treatment facilities but on "Old ash lagoon" of KarGRES-1 situating on the Nura River bank as well. Numerous emergencies and the breakthroughs of the ash lagoon, especially in winter time, resulted in discharge unaccounted contents of mercury waste materials together with ashes of KarGRES-1. Only since 1977 the situation has radically changed, when the local treatment plant for purification of mercury content wastewater has been gone into operation and dispatches of the mercury sludge onto Nikitovski Mercury Combine has been organized. From this moment it became possible if not completely to cease to discharge the mercury into the River Nura, then, at least, to control and to regulate.

Relevant publications:

1. M.A.Ilyushchenko, S.Heaven, T.W.Tanton. Problems of demercurisation of the River Nura in Central Kazakhstan. In book: International Conference on "Problems of Freshwater Mercury Pollution in Natural and Manmade Reservoirs and Possible Ways for their Remediation" (Irkutsk, 13-16 September 2000). Abstracts of Papers. Vinogradov Institute of Geochemistry SB of RAS, 2000, P. 40-41 (Ru & En).
2. S.Heaven, M.A.Ilyushchenko, T.W.Tanton, S.M.Ullrich, E.P.Yanin. Mercury in the River Nura and its floodplain, Central Kazakhstan: I. River sediment and water. The Science of the Total Environment, V. 260, 2000, P. 35-44.
3. S.Heaven, M.A.Ilyushchenko, I.M.Kamberov, M.I.Politikov, T.W.Tanton, S.M.Ullrich, E.P.Yanin. Mercury in the River Nura and its floodplain, Central Kazakhstan: II. Floodplain soils and riverbank silt deposits. The Science of the Total Environment, V. 260, 2000, P. 45-55.
4. T.W.Tanton, E.P.Yanin, S.Heaven, M.A.Ilyushchenko, S.M.Ullrich. Mercury polluted sediments of the river Nura and its floodplain. In book: Mercury as a Global Pollutant - 5th International Conference (Rio de Janeiro, 23-28 May 1999). Abstracts. Rio de Janeiro, 1999, P. 187.
5. M.A.Ilyushchenko, S.A.Abdrashitova, T.W.Tanton, S.Heven, E.P.Yanin. Results of research into mercury pollution of the river Nura in Central Kazakhstan and proposals for demercurisation. "Materials of the Second Congress in memory of B.A.Beremzhanov in

Chemistry and Chemical Technologies" (Almaty 6-8 September 1999). Vestnik KazGU, Chemistry series, No. 5, 1999, P. 18-21. And also: Informational ecological bulletin of the Republic of Kazakhstan. III quarter 1999, P. 57-61 (Ru).

Application:

Table

Output of acetaldehyde and consumption of the mercury on PO "Carbide" in Temirtau City from 1950 to 1997.

Year	Acetaldehyde output	Makeup mercury consumption		Reclaimed mercury consumption		Total mercury consumption	
	thousand tons	t	kg/t	t	kg/t	t	kg/t
1950	1,48						
1951	5,81	23,4	4				
1952	4,47	14,5	3,25				
1953	10,5	20,5	1,96				
1954	13,9	19,7	1,42				
1955	20,8	27	1,3				
1956	36,3	47,2	1,3				
1957	39,6	48,8	1,23				
1958	42,7	52,2	1,22				
1959	40,2	47,6	1,19				
1960	35,6	40,9	1,15				
1961	35,8	40,8	1,14				
1962	37,1	41,9	1,13				
1963	41,7	46,7	1,12				
1964	40,1	44,9	1,12				
1965	45,4	51	1,13				
1966	56,7	66,3	1,17	58,3	1,03	124,6	2,2
1967	63,2	55,5	0,88	62	0,98	117,5	1,86
1968	64,2	54,7	0,85	75,7	1,18	130,34	2,03
1969	61,5	51,8	0,84	71,5	1,17	123,3	2
1970	65	49,8	0,77	81,7	1,25	131,5	2,02
1971	62,1	36,8	0,59	69,9	1,09	106,7	1,72
1972	59,1	28,65	0,49	61,8	1,05	90,5	1,54
1973	68	28,45	0,42	75,6	1,11	104,1	1,53
1974	75,8	31,3	0,41	80,8	1,06	112,1	1,48
1975	77,5	34,5	0,44	73,9	0,95	108,4	1,40
1976	77,56	113,86	1,47				
1977	77	88,33	1,15				

1978	70,4	70,26	1				
1979	70,5	74,35	1,06				
1980	76,59	72,2	0,94				
1981	71,9	67,31	0,94				
1982	72,3	80,17	1,11				
1983	75,6	72,19	0,95				
1984	69,74	74,1	1,06				
1985	60,78	68	1,12				
1986	67,5	70,9	1,05				
1987	65,2	61,15	0,94				
1988	75,37	79,9	1,06				
1989	68,43	81,58	1,19				
1990	64,47	84,2	1,31				
1991	54,93	54,25	0,99				
1992	35,75	35,55	0,99				
1993	23,04	24,62	1,07				
1994	18,05	33,32	1,84				
1995	12,42	22,18	1,79				
1996	9,53	15,4	1,62				
1997	1	2,91	2,9				
Total	2322,62	2351,63					

Comments to the table:

1. The table data were presented to us in 1998 by Matusheva M.F. the chief of a Department of Nature Conservation of PO "Carbide". We are sincerely grateful to her.
2. The plant of thermal regeneration of mercury was in exploitation from 1966 to 1975 inclusively.
3. There is no data on mercury consumption by acetaldehyde production in 1950 in archives of PO "Carbide".