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Mercury Risk Reduction by PowerStation Ash in a River

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ABSTRACT: *The Nura River (the average annual discharge is 0.6 km^3) in Central Kazakhstan is contaminated with mercury downstream of the town of Temirtau as a result of wastewater release from acetaldehyde production lasted for 47 years. About 1 million tons of technogenic silts containing more than 10 mg Hg/kg are deposited along 35-km river section in riverbed, river banks and floodplain. Maximum concentration reaches 420 mg/kg (d.w.). These silts are based on ash of local power plant which discharged ash into the river for most of 47-year period. Nevertheless, concentration of total mercury in river water at the most contaminated section is below 500 ng/L during the most of the year. It exceeds this sanitary standard only during high flood events when Hg is moved by means of sediments' transport. At that concentration of dissolved mercury species does not exceed 20 ng/L. Laboratory tests were conducted to study adsorption of mercury by ash and Hg desorption. Sufficient immobilizing ability of ash was demonstrated. In 2004 Kazakhstan initiated Nura river clean-up project funded by the loan of World Bank.*

The Nura River is an internal river of Central Kazakhstan with a length of 978 km. Its source lies at a height of more than 1000 m in Low-hill region of Kazakhstan. Its average annual discharge is 0.6 km^3 and 80% of it occurs during spring flood. River terminates in the wetlands of Tengiz-Kurgaldzhino depression at a height of about 300 m. River passes on its course three major cities of Central Kazakhstan region. These are industrial centers of Karaganda (population 0.40 million) and Temirtau (populations 0.17 million) as well as new capital of the country Astana (population 0.70 million). The average annual flow of the Nura River in the cross-section of Temirtau is 7.3 m/s, in the cross-section of Astana – 19.4 m/s. Salinity of river water in the cross-section of city Temirtau is 0.6-0.9 mg/l and its pH is 7.2-8.6. Until 1940s the river was the only source of water supply for scarce population of the region mainly occupied in agricultural sector. In order to provide water supply for developing industry in the cities of Karaganda coal-field region started from 1930s two major reservoirs (each has a capacity more than 250 million m^3) were constructed in the basin of the Nura

River. Alluvial groundwater underflow was also widely used. A reservoir with capacity of 410 million m^3 was constructed on river Ishim for water supply of Astana. However these water sources were not sufficient and huge water-basin transfer scheme (Canal Irtysh-Karaganda) was constructed for 13 years to overcome this constraint. The canal has a length of 458 km and designed capacity up to 2 km^3 per year lifting up water from river Irtysh by 416.6 m and delivering it to Karaganda, Temirtau and Astana. The cost of water at the end of the canal reaches 0.5 USD per m^3 [1]. In Soviet time this water was delivered to consumers almost free of charge.

Operation of the canal led to excessive amount of water in the region and as a result irrigation was flourishing both along the canal and in the the Nura River valley. However due to the lack of consumption the actual annual rate of water delivery reached only 1 km^3. After the USSR collapse the government of independent Kazakhstan had to impose a part of the canal's operational costs on the consumers and annual rate of water delivery further decreased to 0.3-0.5 km^3. At present World Bank regards the Nura River as a water-supply alternative to the Canal Irtysh-Karaganda. The rate of regional water consumption is expected to rise which is associated with fast development of new capital of Kazakhstan – city of Astana. However the potential of water supply of Astana using water from the Nura River is limited due to contamination of the river with industrial effluents from upstream cities of Karaganda and Temirtau.

In 2004 the designing phase of the Nura River clean-up Project was started. It is focused on clean-up from mercury which was polluting the river during 47 years as a result of wastewater discharge from the acetaldehyde production of chemical plant "Karbid" which is located in Temirtau and was launched in 1950. For the period of operation the plant consumed 2351.6 tons of mercury. Until 1975 this plant did not have special facilities for wastewater treatment from mercury. The general biological wastewater treatment plant was only designed for treating various types of water-soluble organic matter. According to some data [2] in the mid 1960s concentration of mercury in treated wastewater reached 1.0-50.0 mg/l. At that time Karbide plant often discharged wastewater into the Nura River just after settling in stabilization ponds by-passing the wastewater treatment facilities [3]. The field investigations carried out in the 1990s [4-6] allowed estimating the amount of Hg deposited along 70-km river section downstream the city of Temirtau in soils within the river floodplain, bank deposition of technogenic silts, bottom sediments of riverbed, backwaters and oxbow lakes. The total amount of mercury was estimated as 135 tons.

In 1942 the first turbo-unit of power station KarGRES-1 was launched in Temirtau. By 1950 the capacity of this power station had reached 271 000 kW (the capacity had been doubled by the later 1950s and tripled in the 1960s). Local power-generating coals and flotation wastes of coal-cleaning plants have been combusted at the power station. These materials had the ash content more than 40%. Until 1967 the power station discharged the fly ash to the Nura River at 1 km upstream wastewater outlet of Karbide plant. Concentration of suspended solids in wastewater of KarGRES-1 reached 2.5 g/L according to [7], and 8.5 g/L – according to [2]. After 1967 ash from power plant has been disposed to ash lagoons located in the vicinity of the river. During emergency situation occurring in winter time, ash was still released to the Nura River, and the last event took place in 1997/98. Total amount of ash released to the Nura River can be estimated as 5 million tons.

The typical isotherm curves of mercuric chloride adsorption with ash of Karaganda coal at different levels of pH are given on Fig. 1. They show that adsorption rate decreases at the increase of acidity. Laboratory studies have shown that ash particulates with concentration 10 g/L can fully adsorb mercury from $HgCl_2$ solution with concentration 1 mg/L and natural pH. In case of more concentrated solutions of mercuric chloride ash is capable of the mercury binding up to saturation at 0.7 g Hg/kg.

Ash materials have formed a new type of alluvial depositions within the Nura River known as "technogenic silts" [8]. Their properties significantly differ from natural the river alluvium. Within the first 30 km downstream Temirtau the riverbed is almost everywhere covered with these silts having the typical depth of 1-2 m and reaching 3.5 m at some sites. Along this section of the river the technogenic silts carried away from the riverbed have formed large depositions on the banks (area of about 130 Ha) also reaching a depth more than 3 m. These depositions often contain interlayers of river alluvium. Sometimes they are covered with the 0.5-1.0 m layer of fertile soil overgrown with shrubs.

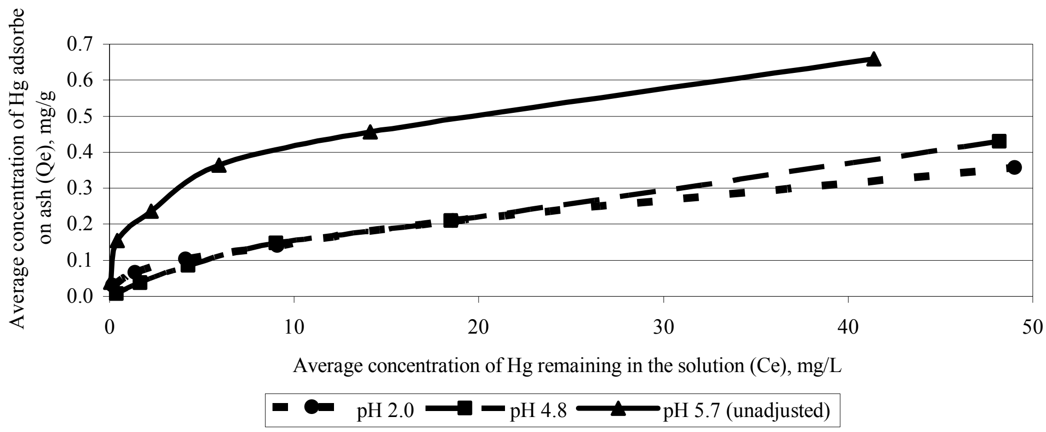

FIGURE 1. Isotherms of mercury adsorption onto power station ash of Karaganda coal at different levels of pH (initial [$HgCl_2$] varied from 0.5 to 50 mg Hg*L^{-1}, C_{ash}=10 g/L, T=25^{0}C, 4-hour experiment)

Technogenic silts deposited near Temirtau have a typical appearance of local coal-fired ash (including bluish color). As going downstream these silts are mixed with big volumes of fertile soil carried away from irrigated fields located within the floodplain. The appearance and color of silts are gradually changing with the distance from the town. The areas and layers contaminated with mercury are clearly associated with presence of ash materials. As a rule the highest content of Hg could be found in silts which look similar to ash. At present about 1 million tons of technogenic silts containing more than 10 mg Hg/kg ("intervention" level adopted in West Europe) are deposited in the riverbed and river banks within first 35-km section downstream Temirtau. Maximum content of Hg in ash materials reaching 420 mg/kg (d.w.) was found in the riverbed. Area within the floodplain of the Nura River having topsoil layer (0-15 cm) containing more than 2.1 mg Hg/kg (sanitary standard value applied in Kazakhstan) occupies 2400 Ha including 600 Ha containing more than 10 mg Hg/kg.

The data gathered during various laboratory experiments [9] and related to desorption of mercury from different ash materials are given at Figures 2 and 3, and Table 1. The curve on Figure 2 shows the effect of leaching solutions of different pHs on mercury (II) freshly loaded onto ash of Karaganda coal from mercuric chloride solution. Even at moderate deviation of pH from neutral level 20% of freshly adsorbed mercury (II) can be leached both at acidic and at alkaline conditions. Same effect is observed at increase of ionic force of neutral solution higher than 0.1 M. Up to 85% of freshly adsorbed mercury (II) is leached from ash of Karaganda coal when washed by 1M solution of either hydrochloric acid or ammonium acetate. Aging of ash with adsorbed mercury (e.g. when drying, see Table 1) leads to significant decrease of chemical mobilizing of Hg (II). Figure 3 shows the curves of mercury desorption from two ash-containing samples of natural sediments from the Nura River originally containing 20 and 117 mg Hg/kg respectively. These curves demonstrate transformation of adsorbed mercury into less mobile forms when ash is being aged. This process protects mercury from noticeable mobilizing in the range of pH 4.5-9.0. These samples also become more resistant to leaching by buffer solutions and mineral acids: less than 2% could be leached by either sodium acetate, or sodium tetraborate, or ammonium acetate; strong mineral acids could leach not more than 45% of mercury. Results given in Table 1 also demonstrate stronger biding of aged ash with mercury (II) in comparison with elemental mercury. Conducted experiments may suggest the chemical nature of mercury immobilization by ash particles. More specifically this process may occur due to the formation of oxide forms of mercury for which there are known several modifications with different chemical stability turning into each other.

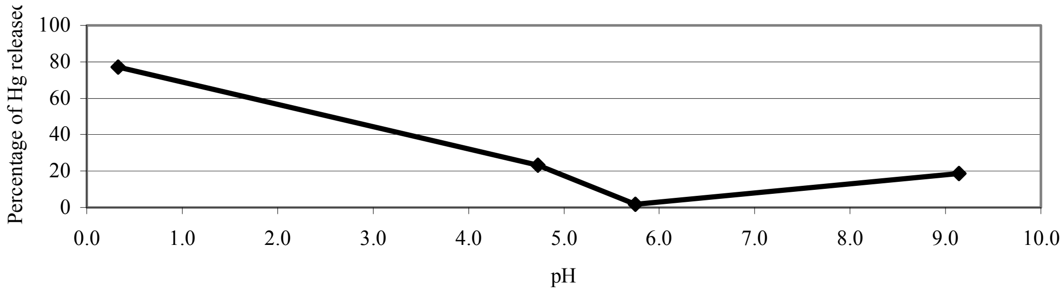

FIGURE 2. Release of mercury from the wet Hg-loaded ash of Karaganda coal at various pHs (C_{ash} = 10 g/L, $C_{Hg\ on\ ash}$ = 82 - 87 mg/kg on dry weight basis, T=25^{0}C, 24-hour experiment)

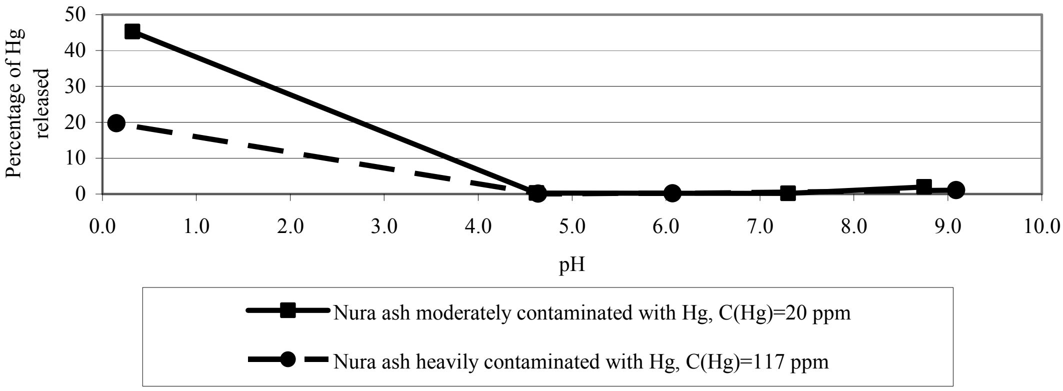

FIGURE 3. Percentage of Hg released at various levels of pH from dry contaminated ashes taken from the Nura River bank deposits (C_{ash} = 10 g/L, T=25^{0}C, 24-hour experiment)

In-situ concentration of total mercury in the Nura River water downstream Temirtau is relatively low. For example, it did not exceed 126 ng/L even at the most contaminated river cross-section (8.2 km downstream the wastewater outlet) in autumn 2001 when the water flow was 16 m^3/s. Only during moderate flood period when the water flow is 100 m^3/s (Table 2) concentration of total mercury in water exceeds sanitary

TABLE 1. Release of mercury from wet and dried Hg-loaded ashes into 1 M ammonium acetate (C_{ash} = 10 g*L^{-1}, T=25^0C, 1-hour experiment)

Type of ash	pH at the end of experiment	Content of Hg in ash, ppm (dry weight basis)	Percentage of mercury leached by 1M ammonium acetate
Wet power station ash of Karaganda coal loaded with $HgCl_2$	6.81	81.5	**85.2**
Dried power station ash of Karaganda coal loaded with $HgCl_2$	6.60	21.0	**15.3**
Dry power station ash of Karaganda coal loaded with elemental Hg vapor	6.52	283.9	**47.3**
Power station ash from bank deposits at the Nura River floodplain (moderate Hg content)	6.60	20.2	**0.2**
Power station ash from bank deposits at the Nura River floodplain (high Hg content)	6.70	117.1	**0.1**

TABLE 2. Concentration of total mercury in surface water of the Nura River during spring flood of 2002, sampling period – April 8-13 (water flow in the cross-section of Temirtau was 70 m^3/s)

Conven-tional distance downstream wastewater outlet in Temirtau, km	Average concen-tration of dissolved mercury, ng/L	Average concen-tration of total mercury, ng/L	Average concen-tration of mercury in suspended solids, ng/L	Average content of suspended solids in water, mg/L	Calculated concen-tration of mercury in suspended solids, mg/kg	pH
0		128.47				
1.8	10.50	304.39	203.5	14.8	13.8	7.24
4.6		894.46				
8.4		1043.56				
14.4		824.17				
18.3	5.02	451.25	383.5	34.7	11.1	7.46
29.7		377.67				
53	4.40	161.96	116.5	34.6	3.4	7.56
71		38.20				
84	2.33	7.93	11.5	28.8	0.4	7.46
109		12.79				
167		8.70				
200		5.45				7.63
252		6.29				
281		4.08		36.4		
236		6.98				
342		4.74				
381		7.38				
467		3.86				

standard value adopted in Kazakhstan (500 ng/L) along 15-km river section. In spring 2004 during the high flood event when water flow was125 m^3/s total Hg concentration reached 4200 ng/l. However at further increase of water flow up to 650 m^3/s Hg concentration became decreasing to the level of 1200 ng/L due to dilution. During high spring floods in 2004 contamination of water exceeded sanitary standards adopted in Kazakhstan along 50-km river section. However when samples were filtered through 0.45-μm membranes total Hg concentration fell to 5-20 ng/l. It is evidence that transport of mercury downstream currently takes place predominantly by means of silt movement and not as dissolved species.

High mercury immobilization with technogenic silts formed on the basis of power station ash made difficult to justify the necessity of treatment of mercury-containing bottom sediments on the World Bank project. In its current status the mercury does not pose evident human health risk for the city of Astana even during high flood events when considerable rearrangement of mercury-containing technogenic silts takes place. However 10 years have passed since local sanitary authorities prohibited water intake out of the Nura River even for technical needs.

In 2004 the official program of mercury monitoring for the river water was initiated by the state for the first time since occurrence of mercury pollution. This program covers the whole river downstream Karaganda and is scheduled for 1 year. For the last 15 years such studies were only done by research teams in the frame of initiative projects funded via international grants. Unfortunately, the official program is relatively limited, e.g. it only assumes determination of total mercury in water and the filtration of water is not anticipated. Total mercury is also determined in a very limited number of samples of fish and bottom sediments. Beside the limited funding the other limiting factor for large-scale studies is a poor equipping of local laboratories with state-of-the-art analytical instruments. For example at present there are no laboratories in Kazakhstan which are capable of determination of methyl mercury concentration in environmental samples. At the same time it is obvious that study of microbial mediated mobilization of mercury in sediments of the floodplain of the Nura River is very important. Similar can be said about the studies of mercury accumulation via food chain because the content of mercury in fish (non-predator species) caught in the river reaches 1.5 mg/kg (w.w.).

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