Removal of Mercury from Contaminated Soils at the Pavlodar Chemical Plant

V. Ye. Khrapunov, R.A. Isakova, B.L. Levintov, P.D. Kalb, I.M. Kamberov, A. Trebukhov

Presented at the REWAS 2004 Global Symposium on Recycling, Waste Treatment and Clean Technology
Madrid, Spain

September 2004

Environmental Sciences Department
Environmental Research & Technology Division

Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

Managed by
Brookhaven Science Associates, LLC
for the United States Department of Energy under
Contract No. DE-AC02-98CH10886

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party’s use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
REMOVAL OF MERCURY FROM CONTAMINATED SOILS AT THE PAVLODAR CHEMICAL PLANT

V. Ye. Khrapunov¹, R. A. Isakova¹, B. L. Levintov¹, P. D. Kalb², I. M. Kamberov¹, A. Trebukhov¹

¹ Institute of Metallurgy and Ore Benefication, Almaty, Republic of Kazakhstan
² Brookhaven National Laboratory, Upton, NY, U.S.A.

Abstract

Soils beneath and adjacent to the Pavlodar Chemical Plant in Kazakhstan have been contaminated with elemental mercury as a result of chlor alkali processing using mercury cathode cell technology. The work described in this paper was conducted in preparation for a demonstration of a technology to remove the mercury from the contaminated soils using a vacuum assisted thermal distillation process. The process can operate at temperatures from 250 – 500 °C and pressures of 0.13kPa - 1.33kPa. Following vaporization, the mercury vapor is cooled, condensed and concentrated back to liquid elemental mercury. It will then be treated using the Sulfur Polymer Stabilization/Solidification process developed at Brookhaven National Laboratory as described in a companion paper at this conference.

The overall project objectives include chemical and physical characterization of the contaminated soils, study of the influence of the soil’s physical-chemical and hydro dynamical characteristics on process parameters, and laboratory testing to optimize the mercury sublimation rate when heating in vacuum. Based on these laboratory and pilot-scale data, a full-scale production process will be designed for testing. This paper describes the soil characterization. This work is being sponsored by the International Science and Technology Center.
Introduction

Impacts of world-wide industrial activities on human health and the environment are ubiquitous. Mercury contamination has been shown to be one of the most toxic types among anthropogenic pollution of the environment.

In Kazakhstan, the territory adjacent to the Pavlodar Chemical Plant (the “PKhZ” OJSC), which is engaged in electrolysis production of chlorine and alkali using the mercury-pool cathode technique, has been an intense source of environmental pollution with mercury. For the period from 1975 to 1993, according to various estimates, the total mercury emission into the environment amounted to 1,394-3,021 tons; the majority of this mercury contamination (over 1,000 tons) has been concentrated in the floors and soils within the boundaries of the Pavlodar Chemical Plant Electrolysis Shop. This has resulted in formation of an anthropogenic mercury deposit, which is comparable to a moderately sized natural deposit of uranium. [1, 2]. The challenge of remediating similar sources of mercury pollution may be successfully accomplished using the vacuum-assisted thermal distillation process as an ecologically clean method of mercury recovery from various types of the raw materials [3-5].

Sampling

Representative samples of the soil were taken from under the concrete base of the Pavlodar Chemical Plant Electrolysis Shop. Specialists from the “PKhZ” OJSC, the Institute of Metallurgy and Ore Beneficiation of the MES RK and the Institute of Nuclear Physics of the National Nuclear Center of Kazakhstan (NNC RK) evaluated previous data and studied the plant layout to choose the proper locations for driving the sampling boreholes and determining their quantity and depth.

Samples were taken from 12 boreholes according to the layout presented in Figure 1, after drilling through the concrete base of Electrolysis Shop #31 of the “PKhZ” OJSC. The depth of the boreholes depended on the groundwater level at the Plant’s site, availability of the underground service lines and concrete bearing supports, and varied from 1.5 to 2.5 m. The sampling was carried out along the entire wall of the boreholes every 0.5 m. 25 samples were taken from each borehole. The samples were thoroughly mixed interval-by-interval and analyzed for mercury content. In all, 300 samples were taken with a total mass of about 600 kg.

Fig. 1 – Layout of the Bore Pits Location in the Boundary of the Former Electrolysis Shop Base
The sample from each borehole was sieved through a screen with the mesh size of 10 mm and then it was divided into two parts by a Johns divider. One half of the sample from each borehole was put into the labeled package while other parts were combined and thoroughly mixed. In such a way about 300 kg of the soil were obtained, out of which the average sample with the mass of 10 kg was taken with the quartering method in order to determine physical-chemical properties of the soil and to carry out the laboratory tests.

**Sample Analysis**

The analytic work for determining the mercury content in the samples of mercury-contaminated soils was performed according to certified procedures using an atomic absorption spectrophotometer AGP-01 and mercury vapor generating system (GPR-1M) ensuring a detection limit of 0.005 mg/kg or $5 \times 10^{-4}\%$. In all, 300 analyses were performed to determine the mercury content. Internal quality assurance checks were executed on 5% of the total number of measurements, and external quality assurance checks were conducted on 10% of the samples by a highly-qualified outside lab using a Perkin Elmer Analist-100.

The results of analyses demonstrated that the mercury content in all boreholes decreases as the sampling depth increases. The samples from boreholes # 2, 6 and 7 had higher mercury concentrations; they contained 19.6±2.11, 19.83±3.61, 31.582±0.31% mercury respectively. Boreholes # 3 and # 10 contain 1.795±0.0248 and 6.296±0.95%. In boreholes # 9 and # 12 the mercury content was 35.5±15 and 49.4±0.3 mg/kg of the soil, and in the rest from 14-6 to 3.8-1.2 mg/kg.

Soil moisture was determined by thermogravimetric method at the temperature of 60°C and pressure of 0.13 kPa, amounted to 9.2%. The angle of repose in the wet material is equal to 39°. The bulk density of the wet material without shaking down is 1.16 g/cm$^3$ and with shaking down is 1.37 g/cm$^3$. The angle of repose in the dry material is equal to 32°. The bulk density of the dry material without shaking down is 1.27 g/cm$^3$ and with shaking down 1.38 g/cm$^3$. The particle size analysis of the dry soil from the “PKhZ” OJSC is given in Table 1.

<table>
<thead>
<tr>
<th>Fraction size, mm:</th>
<th>-10.0+7.0</th>
<th>-7.0+5.0</th>
<th>-5.0+3.0</th>
<th>-3.0+2.5</th>
<th>-2.5+1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield, %</td>
<td>0.3</td>
<td>2.4</td>
<td>4.6</td>
<td>0.32</td>
<td>5.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction size, mm:</th>
<th>-1.6+1.0</th>
<th>-1.0+0.63</th>
<th>-0.63+0.2</th>
<th>-0.4+0.315</th>
<th>-0.315+0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield, %</td>
<td>5.7</td>
<td>9.7</td>
<td>12.41</td>
<td>16.7</td>
<td>19.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction size, mm:</th>
<th>-0.2+0.16</th>
<th>-0.16+0.1</th>
<th>-0.1+0.063</th>
<th>-0.063+0.05</th>
<th>-0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield, %</td>
<td>8.2</td>
<td>8.0</td>
<td>4.9</td>
<td>1.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

It is evident that the soil mainly (about 85%) is presented by fractions with sizes ranging from 2.5 to 0.1 mm.

The chemical analysis of the average sample for mercury content was performed using the titrimetric method in four parallel determinations. The mercury content amounted to: 1.43; 1.54; 1.32; 1.32%. The mean value is 1.4%. The mercury content varied from 1.35% to 0.24% when being defined in five parallel determinations using the AGP-01 device. The chemical analysis of the average sample of soil in mass %: Hg – 1.4; SiO$_2$ – 74.23; Al$_2$O$_3$ – 9.36; CaO – 3.91; Fe$_2$O$_3$ – 2.31; K – 1.65; Na – 1.65. The spectral analysis has also acknowledged that the base
is composed of Si, Al, Ca, Na. In addition, the following elements were detected in 1% Hg, Fe; in 0.1% Mg, Ti, V; in 0.01% Mn, Cr, Cu; and in 0.003% Ni, Pb.

X-ray – phase analysis has detected the following minerals in the sample: quartz, albite (NaAlSi$_3$O$_8$), kaolinite (Al$_4$Si$_4$O$_{10}$(OH)$_8$), the traces of muscovite (KA$_2$(OH)$_2$AlSi$_3$O$_{10}$).

The mineralogical analysis has detected α-quartz, colorless carbonate, possibly calcite (CaCO$_3$), albite, a group of feldspars, ferric hydroxides, and kaolinite. IR-spectroscopy was conducted using a Specord M-80 and the following minerals were identified in the soil: quartz α-SiO$_2$, pyrophyllite Al$_2$[(OH)$_2$/Si$_4$O$_{10}$], halloysite Al$_4$[(OH)$_8$/Si$_4$O$_{10}$(H$_2$O)$_4$] and nephrite Ca(Mg,Fe)$_4$[(OH)$_2$/Si$_4$O$_{12}$].

**Process Optimization**

Laboratory testing of soil samples with a particle size of 10 mm was conducted at the plant to determine the influence of the principal factors on the mercury distillation rate when heating in vacuum. The measurements included periodic weighing of the material and collecting condensate in a special condensate collection vessel that was cooled (see Figure 2).

![Laboratory-Scale Plant With Periodic Weighing of the Weighed Amount of the Material](image)

**Fig. 2 – Laboratory-Scale Plant With Periodic Weighing of the Weighed Amount of the Material**

1 – electric kiln; 2 – quartz reactor; 3 – porcelain boat with a weighed amount of the material; 4 – rubber plug; 5 – heat-insulating shield; 6 – a casing with chromel-alumel thermocouple; 7 – cooler; 8 – rubber seal; 9 – condensate collector.
The soil thermogram taken by Derivatograph Q-1000 at the heating rate of 10 degree/min has been depicted in Figure 3. It can be seen that at temperatures up to 700°C the material is not melted and remains loose, which is important for choosing equipment and facilities for the mercury distillation process.

Fig. 3 – Thermogravitogram of the Representative Sample of the “PKhZ” OJSC Soils

Judging from the residual content of mercury, it is evident (Figure 4) that the rate of mercury distillation during the examined interval has a low dependence on the height of the soil layer and it steadily increases with decline in pressure from the atmospheric pressure to 20 kPa. Under further pressure decline the mercury distillation rate rises sharply. A similar dependence may be observed in case of the temperature rise, particularly above 250°C.

An equally high degree of mercury distillation, i.e., process efficiency (the cinders contain less than 0.001%) can be reached both at 250°C and 0.13kPa, and at 350°C and 1.33 kPa. At a pressure of 1.33 kPa, it is possible to enhance the specific capacity of the process by increasing temperature up to 450-500°C.

The achieved residual content of mercury in the soil cinders meets the European sanitary regulations that allows storage after demercurization in open dumps without burial of the waste. However with output capacities of the vacuum-thermal plant up to 25 tons/day and more, it is likely that some of the residual cinders will exhibit a higher concentration of mercury (>10 mg/kg). These materials can be segregated and treated directly by other means as described below.
Fig. 4. Dependence of the Mercury Residual Content in the Soil Cinders on Conditions of the Vacuum-Thermal Distillation

1 – pressure at 200°C; 2 – time at 200°C and 1.33 kPa; 3 – the layer height at 250°C and 1.33 kPa; 4 – temperature at 0.13 kPa

The analysis of hydrodynamic properties of the soils, which to a considerable degree determine the producing capacity of the conveying system of the vibro-vacuum plant, was carried out on the model of a vertical screw vibrating conveyor at conventional pressure. The vibration frequency was 730-1,460 rpm, the angle of vibration – 30° to the horizon, the vibration amplitude: vertical – 0.8-1.3 mm; horizontal – 1.44-1.58 mm. The test results are given in Table 2. The conveyor capacity may be varied within a wide process range: from 0 to 360 kg/day through changing the vibration parameters within the indicated limits.

Table 2. Conditions and Results of the Vibrating Conveyor Calibration

<table>
<thead>
<tr>
<th>Calibration conditions of the vertical conveyor</th>
<th>Test numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Drive engine load of two-shaft vibrator, V</td>
<td>40</td>
</tr>
<tr>
<td>Vibrator shaft speed (vibration frequency), rpm</td>
<td>730</td>
</tr>
<tr>
<td>Vibration amplitude of the mean diameter point (140 mm) of the vibrating trough</td>
<td>Horizontal, mm</td>
</tr>
<tr>
<td></td>
<td>Vertical, mm</td>
</tr>
<tr>
<td>Conveyor capacity by the soil, kg/day</td>
<td>0</td>
</tr>
</tbody>
</table>

Treatment of Mercury Residuals
After scientific consultations with representatives of the U.S. Department of Energy’s Brookhaven National Laboratory (BNL) a program of joint research has been initiated to treat elemental mercury produced by the thermally assisted vacuum technology and higher mercury concentration residuals from the process. These waste products will be treated using the Sulfur-Polymer Stabilization/Solidification (SPSS) Process developed at BNL to chemically and physically stabilize mercury waste residuals [6]. Under this companion project sponsored by the ISTC and the U.S. Department of Energy Initiatives for Proliferation Prevention Program, a pilot-scale SPSS processing facility will be installed in Pavlodar. Materials for the SPSS process will be manufactured in Kazakhstan from by-product sulfur generated in the production of petroleum. Treated waste is encapsulated in a high-strength, durable sulfur concrete, with low permeability, leachability, and mercury vapor pressure. This concrete product may potentially be used at the “PKhZ” OJSC and other polluted areas as part of a protective shield or barrier to further prevent contaminant migration.

Summary and Conclusions

Based on results to date, the initial data have been prepared for designing and manufacturing a pilot-scale vacuum-assisted thermal distillation plant with a production capacity of 500 kg/day. Application of the SPSS technology for the final treatment of mercury waste after removal and concentration will help to ensure a long-term, safe ecological disposition.

References:


