Limnology and Freshwater Biology 2022 (3): 1312-1314 DOI:10.31951/2658-3518-2022-A-3-1312

SI: «Mercury in Biosphere: Environmental and Geochemical Aspects»

Short communication

ISSN 2658-3518

LIMNOLOGY FRESHWATER BIOLOGY

www.limnolfwbiol.com

Technology for the treatment of mercury-containing wastes

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ABSTRACT. We have developed an efficient and environmentally friendly technology based on a combination of mechanical treatment and chemical immobilization to demercurize mercury-containing waste.

Keywords: mercury-containing wastes, gravitational concentration, chemical immobilization of mercury

1. Introduction

The development of technologies for demercurization of mercury-containing wastes is an extremely urgent problem, as mercury is a known super-toxicant. Mercury pollution in Russia is related to the activity of industrial facilities that produce mercury and its compounds, manufacture mercury-containing products (e.g. light bulbs), or use mercury in production cycles. These facilities produce mercury-containing wastes (MCW) that have the potential to poison the environment.

Moreover, the abrupt closure of companies that have used mercury in production cycles, and, hence, the "abandoned" state of facilities with unused raw materials and other chemicals results in mercury pollution of production buildings and facilities and the environment. In these cases, the prevention of mercury pollution depends mainly on the effectiveness of the technologies used to neutralize mercury-containing waste. Currently, the methods based on the combination of the extraction of metallic mercury from MCW and subsequent conversion of sorbed non-recoverable mercury into an insoluble compound, with the final product not exceeding the fourth hazard class, are considered the most promising and environmentally friendly (Levchenko L.M. 2010, 2012, 2014; Minin V.A. 2015, 2021).

The aim of this work was to develop a technology for the demercurization of solid waste based on gravity separation combined with subsequent chemical treatment. In this technology, metallic mercury is supposed to be extracted with a centrifuge-like equipment, and the non-recoverable mercury is to be converted into mercury sulfide that belongs to the fourth hazard class according to the Russian classification.

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Received: June 15, 2022; ***Accepted:*** July 15, 2022;
Available online: July 31, 2022

2. Materials and methods

2.1 Materials

Mercury-containing waste (MCW) with low mercury content (three or four groups according to the national standard GOST R 52105-2003) was used to develop a technology for the demercurization of solid waste. The technology was developed based on the requirements of GOST 12.3.031, taking into account that, according to the requirements of GOST 17.2.3.02 and GOST 12.1.005, the developed technology should ensure the conversion of mercury or its compounds into low volatile and low soluble states.

The MCW used were soils, construction debris, metal parts, and other materials generated from the removal of buildings and facilities where mercury production cycles were conducted. All industrial wastes containing mercury are classified as extremely hazardous wastes (Hazard Class I) according to the Federal Waste Classification Catalog (approved by the Order of the Ministry of Natural Resources of Russia dated 02.12.2002 No. 786). Most of the MCW were construction wastes: fragments of various sizes resulting from the destruction of reinforced concrete and bricks or other parts of buildings and their plastered surfaces. Soils heavily contaminated with mercury were materials of various grain sizes, in which mercury was present in the form of liquid droplets. The coarse clastic fraction consisted of crushed stone and construction debris fragments; in this part, the mercury content was close to the MPC. The fine-grained fraction consisted of clay-sand material, in which most of the mercury was accumulated (> 100 MPC). Metallic mercury and its compounds were present in this material as fine particles in a "free" or adsorbed state. The bulk density ranged from 1.5 t/m^3 (gypsum and soil) to 3.0 t/m3 (reinforced concrete), depending on the composition of the waste.

2.2. Methods used

The following methods were used in this study to determine mercury concentrations and the component composition of MCW.

Powder diffractograms of MCW were recorded using a Shimadzu XRD-7000 diffractometer. The IR transmission spectra were recorded in the range of 350 to 4000 cm-1 using a Fourier IR spectrophotometer SCIMITAR FTS 2000 series (DIGILAB). Samples for the FTIR studies were prepared by mixing and grinding 1.0 mg of sample with 3 g of dried KBr, followed by tableting.

The analysis of mercury concentration in MCW was carried out by the AAS method (Yuliya analyzer) in accordance with GOST Z 51768-2001 and PNDF 14.1.2.20-95. The microelement composition of the studied MCW samples was characterized using atomic emission spectrometry with arc excitation (DPT AES). The analysis was performed using a PGS-2 spectrometer (Carl Zeiss Jena, Germany) with a diffraction grating as a dispersion element and a photodiode array to record the spectra. A double-lens slit illumination system with 20μm width was used. The magnitude of the arc discharge current was 10 A, and the exposure time was 18 seconds. Prior to analysis, the electrodes were cleared of surface contamination by preignition at a current of 12 A for 20 seconds.

3. Results

3.1. Material composition

Typical production waste (construction waste and soil) was powders, various colors from brick to dark brown. In the diffraction patterns of RSO powders (construction waste and soil), only the crystalline phase of SiO_2 was detected. Waste composition based on chemical analysis, % wt.: silicon oxide - 92; aluminosilicates 6-8; mercury - 10-0.0004; iron - 0.1; calcium - 0.1; magnesium - 0.3; manganese - 0.1, and titanium - 0.15.

In the IR spectra, intense bands were observed in the region of 1084-1036 cm-1, which corresponds to the stretching vibrations of Si-O. Additionally, the presence of water was observed; absorption bands were recorded in 3437 cm-1 and 3432 cm-1, which was related to the stretching and bending vibrations of H_2O. In soil samples, calcium hydroxide (3618 cm-1) was also observed. In the region of 600-400 cm^{-1}, oscillations of the aluminosilicate frame appeared. Vibration bands in 420-534 cm^{-1} were vibrations of the SiO_4 layer, tetrahedra. Bands in 797 cm^{-1} and 779 cm^{-1} were bending vibrations of Si-O. The absorption bands in 1422–1432 cm^{-1} and the shoulder in 876 cm^{-1} referred to vibrations of the C=O bond in carbonate. Quartz, aluminosilicates, carbonates and calcium hydroxides represented the mineral composition of RSO (construction waste and soil) was represented.

To determine the mercury concentration in RSO, the method of dissolving mercury in nitric acid was used. The procedure was as follows: five parallel weighings of 1 g of soil (G1-G5) were repeatedly washed alternately with nitric acid and water, then the washing solutions were brought to the mark in volumetric flasks of 100 ml. For analysis, the resulting solutions were diluted 5000 times. The mean mercury concentration in the soil determined by the AAS method was 3.94 ± 0.40 mg/g. In WRS samples, mercury concentrations varied from 0.05-0.06 mg/g to 50-60 mg/kg, while the MPC level for soils was 2.1 mg/kg, i.e. there was an excess of MPC.

3.2. RSO demercurization technology

The technological scheme for the neutralization of RSO is based on the gravitational method of separation of metallic mercury in water and the method of chemical immobilization of mercury in a pilot plant. According to the scheme, construction waste and soils initially pass through two stages of crushing (jaw and roller crushers); in the case of large blocks of construction waste, additional separation is carried out in a butare. Crushed material with a particle size of less than 2 mm from the crusher in the form of pulp is supplied by a sand pump for gravity enrichment to the Itomak KG-2.0 centrifugal concentrator with the production of metallic mercury, concentrate, cake and tailings. The concentrate is used to isolate metallic mercury, and the remaining tails and cake after filtration are immobilized in two stages: oxidation and the formation of mercury sulfide in waste. The enrichment tailings are constantly washed and transported by the stream into a transfer tank with a volume of 0.2 m^2 and are fed for dehydration by the PVP 12.5 / 12.5 sand pump, while the concentrate remains in the conical bowl and is periodically unloaded into the concentrate tank, from where it enters for finishing at the concentration table SKO-0.5. Cake, material dehydrated to 20-30% moisture content, is removed with a knife device from the surface of the drum fabric into a receiving funnel and then enters the immobilizer into the mercury immobilization apparatus through the chute, in which the process of chemical immobilization of mercury adsorbed on the surface of construction waste is carried out. From the container, the decontaminated waste is reloaded into the container; samples are taken from which the hazard class of the waste is determined.

4. Discussion

We have demonstrated that the MCW processing consists of four stages. Stage 1. Mercury contaminated soils, wastes or sludges are separated according to their size (particles larger than 2 mm and smaller). Particles from the larger fraction are crushed to a size of less than 2 mm, then particles from both streams are combined and processed into slurry. Stage 2. The slurry enters the gravity separator (series ITOMAK KG) where metallic mercury is extracted by gravity separation. Stage 3. The slurry separated from metallic mercury is sent to the reactor for chemical immobilization of the remaining mercury with calcium polysulfide. Stage 4. Dehydration of the slurry with a filter press. The cake is taken to the MCW landfill as waste of hazard class IV -V, and the water is returned to the technological process, with the aspiration system ensuring that possible mercury vapor emissions in the work area and beyond are removed and neutralized.

The mercury remaining after gravitational separation is chemically inactivated by converting it to the ionic form (Hg^{2+}) with an oxidant containing active chlorine and then treated with a solution of calcium polysulfide. The resulting compound, mercury sulfide, HgS(II), is sparingly soluble and volatile and does not pose an environmental hazard.

The technological performance indicators of the treatment plant are as follows: maximum productivity for the feedstock up to 0.2 t/h; maximum fineness of the source material is 70 mm; circulating water supply, maximum water consumption of the process water, m3/h; maximum power consumption (3 x 220/380V, 50Hz), kW 55.6; outside air temperature +1°C - + 45°C.

5. Conclusions

The processing 500 kg of processed soils and 800 kg of processed construction waste revealed that MCW demercurization technology enabled extraction of up to 98% of metallic mercury from soils and up to 80% from construction waste.

The residual amounts of mercury in construction waste and soils were converted into low- soluble mercury sulfide using a solution of calcium polysulfide whereupon the content of unbound mercury in the water extracts from the demercurized samples turned out to be below the detection limits of the AAS method (0.0005 mg/l). According to the results of biotesting, the demercurized wastes were classified as hazard class IV wastes.

Ackhowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, NIIC SB RAS No. 121031700321-3.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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