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Neutralization of Arsenic Wastes from Mining and Metallurgical Industry

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Abstract—The authors deal with the problem of pollution of the town of Svirsk (Siberia, Russian Federation) with toxic wastes from mining and metallurgical industry. Areas of heavy metal pollution of superficial soil layers are established. The principal technological approaches to neutralization of the pollution source are presented.

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A special complex of urgent problems is associated with the formation and accumulation of toxic wastes—one of the most dangerous consequences of human activities with great environmental and human health impacts. Arsenic-containing wastes from mining and metallurgical industry pose an extreme threat in view of the fact they can preserve activity, specifically ability for chemical transformations and migration under natural conditions, for a very long time.

Arsenic-containing products were mostly consumed in defense industry. In late 1940s and early 1950s, the demand of defense industry for arsenic compounds sharply decreased, and a number of enterprises were closed. However, the production sites of these enterprises were not disposed properly.

An example is provided by the production site of the former Angarsk metallurgical plant (AMP) on processing of arsenopyrite ores from the Cheremkhovsky District, Irkutsk Region. The wastes stored at this site include arsenic-containing compounds and a wide variety of heavy metal compounds. The situation is worsened by the fact that this production site is located in a close proximity to a populated area and at a distance of 600 m from the Angara River, thus being a potential social and environmental hazard for the entire territory of the upper part of the Bratsk Basin. As a consequence, the highest death rates in the Irkusk Region (20%) have been recorded here over the years [1].

In this connection, the "Disposal of the Arsenic Pollution Focus at the Production Site of the Angarsk Metallurgical Plant (AMP) in the Region of the Town of Svirsk" was developed and included in the "National System of Chemical and Biological Safety of the Russian Federation (2009–2013)" Federal Targeted Program and the "Environmental Protection in the Irkutsk Region" Regional Program for 2006–2015.

From 1934 to 1949 the AMP produced arsenic trioxide (As_2O) from the arsenopyrite concentrates from the Darasun and Zapokrov ore fields situated in the Zabaykalsky Krai. Arsenic trioxide was produced by a simplified technology involving hearth roasting of the concentrates, trapping arsenic sublimates in coolers, and arsenic trioxide refinement. In 1949 the arsenic production was terminated, and the plant and equipment were depreciated and, in essence, abandoned without appropriate disposal.

The total weight of cinder wastes which still remain at the AMP production site is estimated at 140 thsd ton. These wastes are located in an irregularly shaped stockpile 170 m × 170 m × 7 m in dimensions. In the immediate vicinity of the stockpile, there are debris of the production facilities and remnants of the engineering equipment, a total of 6 thsd ton with the total arsenic content of 150 ton.

According to geoenvironmental survey data, the arsenic and heavy metal soil dispersion areas at the territory of the AMP production site have an ellipsoid shape (200 m × 400 m). The soil concentrations of pollutant metals at the production site are as follows: As 10–4000 MAC_{soil}[1] (MAC_{soil} 2 mg/kg), Sb 30–200

[1] (MAC_{soil}) Maximum allowable concentration in soil.

Element concentrations in the filtrates of AMP wastes as determined by inductively coupled plasma–mass spectrometry analysis

Element	Element concentrations in the samples, mg/dm^3										
	1	2	3	4	5	6	7	8	9	10	11
S	65.0000	112.000	73.0000	97.200	60.600	88.700	51.200	84.6000	81.500	47.600	47.400
Mn	0.0002	0.001	0.0005	0.005	0.130	0.008	0.008	0.0240	0.013	0.024	0.021
Fe	0.0050	0.004	0.0160	0.023	0.120	0.025	0.140	0.0700	0.060	0.150	0.160
Cu	0.0040	0.003	0.0050	0.002	0.003	0.003	0.008	0.0270	0.008	0.060	0.050
Zn	0.1100	0.013	0.0060	0.080	0.490	0.190	0.300	0.2800	0.250	0.700	0.680
As	0.8400	2.990	3.7800	5.620	4.860	5.390	4.120	4.8700	4.900	8.910	8.980
Sb	0.0083	0.010	0.0260	0.017	0.003	0.014	0.011	0.0110	0.013	0.070	0.090
Pb	0.0015	0.001	0.0011	0.003	0.004	0.004	0.005	0.0020	0.004	0.006	0.005

MAC_{soil} (MAC_{soil} 4 mg/kg), Pb 10–300 MAC_{soil} (MAC_{soil} 32 mg/kg), Cu 3–90 TAC_{soil}[2] (TAC_{soil} 33 mg/kg), Zn 10–130 TAC_{soil} (TAC_{soil} 55 mg/kg) [2]. The arsenic concentration in soil at the territories of the town and gardening facilities, as well as adjacent forest–steppe zone are > 4–150 MAC_{soil}, implying that the pollution

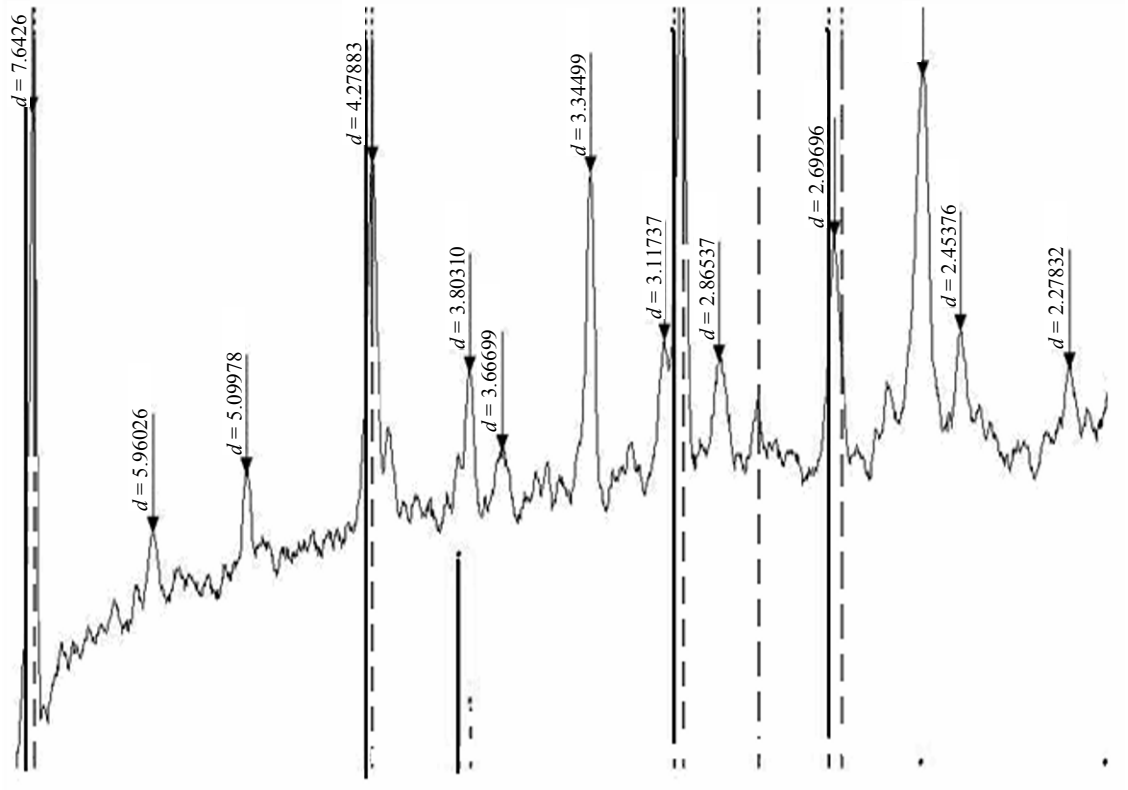

Fig. 1. X-ray diffraction pattern of sample 4: (dashed vertical lines) gypsum $CaSO_4 \cdot 2H_2O$ reflexes; (solid vertical lines) pharmacolite $CaH[AsO_4] \cdot 2H_2O$ reflexes. The gypsum and pharmacolite reflexes were taken from the Powder Diffraction File of the International Centre for Diffraction Data. (*d*) Interplanar spacing, Å.

[2] (TAC_{soil}) Tentative allowable concentration in soil.

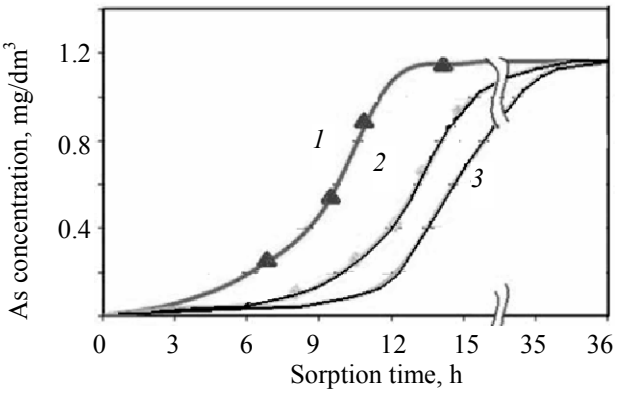

Fig. 2. Kinetic curves of arsenic sorption from washing waters on activated carbon sorbents: (*1*) SKT; (*2*) KAD; and (*3*) Norit RO 3520.

dispersion toward the Angara River and the residential area of the town of Svirsk occurs due to the North–West wind deflation of fine dust from arsenic-containing cinders.

The second source of environmental pollution is associated with washing-out of migration forms of heavy metals from the abandoned engineering equipment by atmospheric precipitates or snowmelt waters, which entails leakage of the pollutants into subsoil levels. Taking into account that the natural washing-out of arsenic from wastes has been lasted for more than 60 years and based on the results of research on the washing-out process, we can state that arsenic has deeply penetrated into porous waste structures and formed diverse links with their components.

We performed an experimental study to gain insight into the mechanism of neutralization of arsenic and heavy metals in the AMP wastes. Samples of production wastes were prepared using cinders (76.6%), soils from the production site (20%), bricks (3.1%), and scraps from arsenic trioxide half-products (0.3%). The samples were treated with a 5% solution of lime milk (CaO 20–200 g/kg) and placed into a chemical reactor to prepare a technological mixture. After a constant pH (pH = 9) has established, the mixture was filtered off, and the filtrate was analyzed for arsenic and heavy metals (see table). Simultaneously, the samples non treated with lime milk were analyzed. It was found that the concentrations of arsenic and heavy metals in the filtrates from neutralized samples (samples 1–9) are 2–5 times lower that in the filtrates from untreated samples (samples 10 and 11), whereas the sulfur concentrations in the

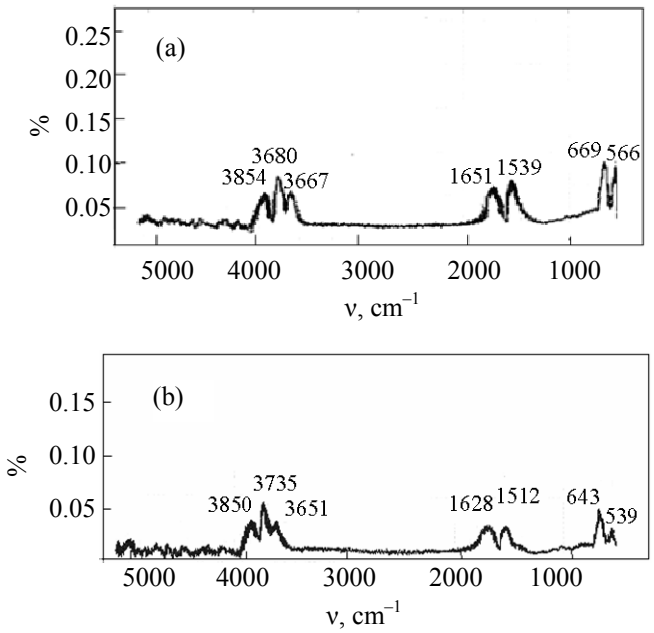

Fig. 3. IR reflection spectra of the surface of the Norit RO 3520 sorbent (a) before and (b) after sorption.

latter samples are 1.5–2 times higher. The lower sulfur concentrations in treated samples can be explained by the results of their X-ray phases analyses.

The asymmetry and shifting to lower angles of certain lines of calcium sulfate hydrate (gypsum) in the X-ray diffraction patterns of the samples (Fig. 1) suggest substitution of sulfur by arsenic to form a poorly soluble compound pharmacolite $CaH[AsO_4]\cdot 2H_2O$. In this case, the function of gypsum in the waste neutralization process is to concentrate arsenic.

The solubility of wastes after neutralization becomes lower by a factor of 8. The optimal concentration of CaO in the lime milk used for waste treatment is 140 g/kg; however, a small part of arsenic (up to 1.6 mg/dm^3) passes into the spent solution.

To exclude the possible environmental pollution with migration forms of arsenic, an improved technology of neutralization of arsenic-containing wastes has been developed. The proposed technology involves sorption purification of wastes to regulated limits (MAC_{fwb}[3] 0.05 mg/dm^3) followed by dumping in a special containment.

[3] (MAC_{fwb}) Maximum allowable concentration in fishery water bodies.

Figure 2 presents the kinetic curves of arsenic sorption from washings from neutralized AMP wastes on different types of activated carbons. The best results were obtained on Norit RO 3520. The protective power time of this sorbent is 3.3 and 1.4 times longer compared with SKT and KAD activated carbons, respectively.

The Norit RO 3520 sorbent has a layered structure similar to that of graphite, and such structure make possible two parallel sorption mechanisms: adsorption and sorbate diffusion into the interlayer space of the sorbent.

The IR reflection spectra of the Norit RO 3520 sorbent after sorption reveal attenuation and shifting of the bands at 570, 670, 1540, and 1650 cm^{-1} (Fig. 3), related to bending vibrations of the carboxylate COO^- group [3].

The COO^- groups on the sorbent surface form two types of bonds with cationic arsenic species $[As(OH)_2^+$, $AsOH]^{2+}$, As^{3+}. The bands in the region of 643 cm^{-1} are assignable to the coordination bonds that are closer to covalent and those in the region of 1512 and 539 cm^{-1}, to the coordinations bonds that are closer to ionic. In the IR reflection spectra of the sorbent after sorption, a shift of the band at 3680 cm^{-1} assignable to vibrations of the OH^- group which, due to its oxygen lone pair, too, can coordinate with cationic arsenic species.

Unlike cations, anionic oxygen species ($H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}) have a larger size (>5 Å) and cannot freely diffuse into the crystal lattice of the sorbent. Presumably, in this case sorption occurs by ion exchange between anionic arsenic species and the hydroxo group of the sorbent. Evidence for this assumption comes from the fact that the pH of the sorbate increases from 3.7 to 5.9.

Thus, the sorption mechanism of ionic arsenic species involves formation of chemical bonds with the surface of the sorbent, sorption in the interplanar space of its crystal lattice, and an ion-exchange reaction.

The arsenic concentration in washings of the post-treatment sorbent is below $MAC_{fwb,}$ which allows them to be used for process needs in the technology of neutralization of AMP wastes.

The estimated environmental effect of preventing soil pollution with heavy metals in this case is RUB 256 mln. A reduced carcinogenic risk is predicted.

Thus, the realization of the "Disposal of the Arsenic Pollution Focus at the Production Site of the Angarsk Metallurgical Plant (AMP) in the Region of the Town of Svirsk" in the framework of the "National System of Chemical and Biological Safety of the Russian Federation (2009–2013) " Federal Targeted Program will allow solution of an urgent environmental and social problem, thereby contribution much to ensuring environmental safety and sustainable economic and social development of the Baikal region.

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