Safe and ecological performance of mining and processing industry

KA Kovalenko
Chinakal Institute of Mining, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
E-mail: kovalenko-ksusha@mail.ru

Abstract. Mineral mining and processing activities result in highly toxic arsenic-bearing waste water discharged in natural water bodies. The promising methods of arsenic removal from waste water use adsorption at natural sorbents and oxidizers. The tests of arsenic removal by adsorption at magnesium- and manganese-bearing minerals show that the use of these natural raw materials can greatly enhance efficiency of the environmental activities in the mining and processing industry.

1. Introduction
In the current conditions of large-scale and high-rate extraction of minerals from the earth, mining industry has to engage itself in processing of low-grade material, with high content of impurities. In the course of mining, beneficiation and metallurgical processing, these impurities concentrate in wastewater, tailings, process solutions and dump waste products. Specific problem is constituted by arsenic compounds which are unavoidable impurities present in crude heavy, nonferrous and noble metals (Table 1). Arsenic content of sulfide gold ore may reach 20% [1]. When ore contains much As, it mostly goes to waste after processing (80% and more). For instance, As content of tin ore is 2100 g/t, which totally goes to tailings, while polymetal sulfide minerals contain up to 1000 g/t As and only 200 g/t As is discarded with waste. Even much more As is thrown away in extraction and processing of gold ore [2].

Table 1. As content in basic commercial minerals, wt%

| Mineral          | Formula          | As    | Mineral          | Formula          | As    |
|------------------|------------------|-------|------------------|------------------|-------|
| Arsenopyrite     | FeAsS            | 46.0  | Chloantite       | NiAs₃           | 73.5  |
| Arsenoferrite    | FeAs₂            | 72.8  | Chatamite        | (Fe, Ni)As₃₋₂   | 70.1  |
| Red arsenic      | As₄S₄           | 70.1  | Gersdorffite     | NiAsS           | 45.3  |
| Orpiment         | As₅S₃           | 61.0  | Cobaltite        | CoAsS           | 45.2  |
| Scorodite        | FeAsO₄·2H₂O     | 49.8  | Smaltite         | Co₃As₂₋₁       | 63.4–71.6 |
|                  |                  |       | Skutterudite     | Co₃As₃         | 73.0–76.4 |
|                  |                  |       | Ni-skutterudite  | Ni₃As₃         | 75.4–76.1 |
|                  |                  |       | Proustite        | Ag₃AsS₃        | 15.2  |
|                  |                  |       | Enargite         | Cu₃AsS₄        | 19.1  |
|                  |                  |       | Tennantite       | Cu₃AsS₃        | 17.0  |
2. Arsenic removal from waste water: a process flow chart

High As concentrations are observed in case of ore oxidation upon exposure and contact with air. Acid arsenical mine water, highly aggressive relative to metals and concrete, is discovered in ore fields Gai, Degtyarka, Karabash, Kochkar and Blyava in the Ural, East Kounrad in Kazakhstan and Khovu-Aksy in Tyva [3]. Process water from copper mines in the Ural (e.g. Gai etc.) contains about 0.4 g/dm³ As and has pH in a range of 2.5–3. Released As during metal ore production poisons the vegetable world. For instance, many unvegetated sites are observed in the copper mine areas in the South Ural and in Kazakhstan [4].

As concentrations range from 0–0.8 to 2–3 mg/dm³ in mine effluents [5, 6], 0.02–0.35 mg/dm³ in effluents of lead and lead–zinc mills and from 0.5 to 0.7 mg/dm³ in effluents of copper and copper–molybdenum mills. Low As concentrations (from 3.5 to 50 mg/dm³) are recorded in waste eater of copper–tungsten, tungsten and molybdenum–tungsten mills. Arsenic concentration in effluents of copper, copper–zinc and polymetal ore mills vary in a wide range from 1.5 to 15 000 mg/dm³. The runoff volumes range widely, too, from 4–5 (titanium–magnesium mills) to 40 000 m³/day (lead melting) [1, 5–7]. Water from tailings ponds is of no lesser concern. Wash liquors after fume cleaning before sulfuric acid production contain much arsenic. Such liquors impure with sulfuric acid, suspended matter and As compounds are no more serviceable. Aiming to minimize effluent discharge, sluicing process involves a closed gas scrubbing circuit, with fewer effluence with higher concentrations of H₂SO₄ (to 40 g/dm³) and As (to 10 g/dm³).

Arsenic is an element less demandable as against its manufacturability. Currently, neither mining nor processing industry can boast completely waste-free and environmentally safe technologies. So far high-toxic As compounds keep entering natural water bodies with industrial effluents. Vast areas of As-containing mineral mining and processing become polluted (Yakutia, Siberia, Transbaikal, Central Asia, Kazakhstan, Ural, Caucasus and Chukotka), which calls for immediate actions to scale down toxicant concentrations in natural and waste water.

Water systems contain arsenic mostly as arsenate (V) and arsenite (III). As (III) compounds are more toxic and their removal presents more difficulties as against As (V) compounds. Therefore integrated waste water treatment should be preceded with preliminary oxidation of As (III) to As (V). In view of high toxicity and limited demand of arsenic compounds, arsenic-bearing water neutralization should ensure production of end solution to comply with sanitary standards (As MAC 0.05 mg/dm³ in fishery water bodies and 0.01 mg/dm³ in potable water), with As concentration in low-toxic and hardly soluble residuum suitable for disposal. Nowadays there is a keen interest in the technologies of sorption with natural materials. These materials possess larger specific surface and relatively high sorption capacity, and are ten times cheaper than artificial adsorbents, thus, they allow avoiding the regeneration stage.

Long-term studies of magnesium and manganese-containing minerals at the Institute of Mining have revealed:

1. Extractability of arsenic (III) and (V) by adsorption at natural mineral from the class of hydrogen oxides—brucite Mg(OH)₂. The resultant filter effluents meet sanitary standards, and the residue is hardly soluble and is disposable. Thermal treatment of natural brucite enhances its adsorption capacity relative to arsenic compounds at reduced consumption of the sorbent [8]. Table 2 describes adsorption capacity of brucite and some other known sorbents relative to arsenic [8–14]. Evidently, both natural and modified brucite exhibits increased adsorption activity relative to the toxicant as compared with the other sorbents listed.

2. Manganese ore of different genesis, containing manganese oxides, show both adsorption and oxidation activity toward arsenites [8, 15, 16]. This property makes it possible to enhance removal of arsenic. The tests of manganese ore from four Siberian deposits (Durnovskkoe, Porozhnaya, Usa and Selezen) show that adsorption capabilities of ore after pre-treatment are much higher (Figure 1).
Table 2. Adsorption capacities of brucite and some other sorbents relative to arsenic compounds

| Sorbent | Consumption, g/dm³ | Initial As concentration, mg/dm³ | Adsorption capacity, mg/g |
|---------|--------------------|---------------------------------|---------------------------|
|         |                    | As (III) | As (V) | As (III) | As (V) |
| Brucite: |                    |          |        |          |        |
| natural | 4                  | 4        | 1–100  | 46–60    | 13–21  |
| modified| 1                  | —        | 20.12  | —        | 0.68   |
| Iron-coated zeolite | 33.3 | —        | —      | —        | —      |
| Zeolite tuff: |                |          | 0.1–4  | 0.0048   | 0.1    |
| ZMA     | —                  | 0.0028   | 0.025  | 0.1      | 0.05   |
| ZME     | —                  | 0.017    | 0.1    | 0.003    | 0.066  |
| ZMS     | 0.002              | 0.05    | 0.002  | 0.002    | 0.006  |
| ZMT     |                    | 0.003    | 0.05   | 0.003    | 0.066  |
| ZH      |                    | 0.002    | 0.05   | 0.002    | 0.006  |
| Clay minerals: |              |          |        |          |        |
| kaolinite | 76                | 0.4     | 0.09   | 0.02     | —      |
| montmorillonite | 76 /19 | 8       | 0.1    | 0.09     | 0.19   |
| Hematite | 40                | 0.02    | 0.02   | 0.02     | —      |
| Industry waste: |             |          |        |          |        |
| red mud | 20                | 0.663   | 0.514  | 28       | —      |
| ash     | —                  | —       | —      | —        | —      |

Figure 1. Adsorption capacity of natural and treated manganese ore relative to arsenic.

Samples of the Usa and Porozhnaya ore were calcinated at \( t = 600 \) °C up to decomposition of carbonates. Suchwise treated minerals have poorly crystallized and imperfect structure, and features high content of active centers, which means high adsorption and oxidation capabilities. The X-ray structure analysis shows that all manganese compounds (gray manganese, rhodochrosite) in the Porozhnaya ore have turned into bixbyite (Mn₂O₃). In the Usa ore, rhodochrosite gets totally converted into hausmannite (MnMn₂O₄). We can say that thermal treatment of these ore types has activated their oxidation ability. The content of manganese in the Porozhnaya and Usa ore is 46% and 22.2%, respectively. Ore from the Durnovskoe and Selezen deposits was subjected to magnetic separation. The latter increased manganese concentration from 16.36 to 36.53% in the Durnovskoe ore and slightly, from 21.25 to 26.71%, in the Selezen ore.

From the experiments with model solution and actual effluents [8, 15–18], the process flow charts have been designed for removal of arsenic from waste water by absorption using magnesium- and manganese-bearing minerals (Figure 2). The proposed process flow allows using standard equipment for water treatment in adsorption.
Figure 2. Process flow charts of arsenic removal from waste water by adsorption on brucite and manganese ore in (a) dynamics and (b) statics: 1—neutralizing agent; 2—doser for brucite; 3—neutralization cell; 4—separation of residue; 5—adsorption brucite filter, or oxidizing filter with manganese ore; 6—doser for brucite or manganese ore; 7—mixing facility cell.

Mining and processing waste water contain acids. Average runoff should be neutralized in order to preclude violation of biochemical processes in water bodies and to prevent corrosion of metallic structures of sewage works. Brucite possesses alkalinity, and, for this reason, it is suggested to use brucite for neutralization of acid waste water. Unlike other common chemical agents (soda and lime), brucite gradually neutralizes acids up to the maximum pH of 9–10.5. Neutralization process with brucite is free from considerable heat emission, and there is no risk of production of high alkalinity solution in case of wrong dosage of the agent. Owing to lower molecular weight, magnesium hydroxide liberates more ions than caustic soda and caustic lime: 1 t NaOH is equivalent to 0.73 t Mg(OH)2 and 1 t Ca(OH)2 is equivalent to 0.79 t Mg(OH)2 [19].

According to the experimental results [17], even during neutralization, correctly selected input of brucite can result in complete precipitation of As. The As-free treated solution can, as a rule, contain considerable concentrations of ion of nonferrous heavy metals (copper, zinc, etc.), and they can selectively be adsorbed at brucite [18]. Then, the residue is processed using any known techniques to return metals to the production cycle. In case the post-neutralization effluents have As content higher than the sanitary code, the waste water is subjected to extra treatment using brucite or manganese ore depending on the toxicant content and form of occurrence.

3. Conclusions
The process flow chart designed and proposed for arsenic removal from waste water by adsorption at brucite and manganese ore provides:
— fine purification of effluents and removal of arsenic and other toxic impurities;
— precipitation of arsenic in disposal residue;
— selective recovery and re-cycling of nonferrous metals;
— recycling of arsenic-free waste water, or discharge after additional treatment if necessary.
Finally, this paper proposes a solution to the relevant problem connected with detoxication of arsenic-bearing water using highly efficient natural sorbents and oxidizers, to enhance environmental activity and performance of the mineral mining and processing industry.

References
[1] Naboichenko SS 2004 Arsenic in Nonferrous Metallurgy Yekaterinburg: UrORAN (in Russian)
[2] Ivanov VV 1996 Ecological Geochemistry of Elements: Reference Book Book 3: Rare p-Elements Moscow: Nedra (in Russian)
[3] Gamayurova VS 1993 Arsenic in Ecology and Biology Moscow: Nauka (in Russian)
[4] Sotnikov VI 1997 Environmental impact of mineral deposits and their development Sorosovskii obrazovatelnyi zhurnal No 5 pp 62–65
[5] Milovanov LV 1971 Wastewater Treatment in Nonferrous Metallurgy Moscow: Metallurgiya (in Russian)
[6] Belevtsev AN, Belevtsev MA and Miroshkina LA 2007 Theory of Environment Protection. Water Pollution Control in Metallurgy: MISIS Teaching Aid No 229 Moscow: Ucheba (in Russian)
[7] Grigoryan VZ 1972 Removal of arsenic from washing solutions of vitrol works Tsveyne Metally No 3 pp 54–56
[8] Bochkarev GR, Pushkareva GI and Kovalenko KA 2010 Natural sorbent and catalyst to remove arsenic from natural and waste waters Journal of Mining Science Vol 46 No 2 pp 197–202
[9] Jeon C-S, Baek K, Park J-K, Oh Y-K and Lee S-Do 2009 Adsorption characteristics of As (V) on iron-coated zeolite Journal of Hazardous Materials Vol 163 pp 804–808
[10] Elizalde-Gonzalez MP, Mattusch J and Einicke W-D 2001 Sorption on natural solids for arsenic removal Chemical Engineering Journal Vol 81 pp 187–195
[11] Elizalde-Gonzalez MP, Mattusch R and Wennrich P 2001 Morgenstern Uptake of arsenite and arsenate by clinoptilolite-rich tuffs Micropor. Mesopor. Mater Vol 46 No 2–3 pp 277–286
[12] Altundogan HS, Altundogan S, Tumen F and Bildik M 2002 Arsenic adsorption from aqueous solutions by activated red mud Waste Manage. Vol 22 pp 357–363
[13] Diamadopoulos E, Ioannidis S and Sakellaropoulos GP 1993 As (V) removal from aqueous solutions by fly ash Water Research Vol 47 pp 30–35
[14] Singh DB, Prasad G, Rupainwarr DC and Singh VN 1988 As (III) removal from aqueous solution by adsorption Water, Air, and Soil Pollution Vol 42 pp 373–386
[15] Bochkarev GR, Pushkareva GI and Kovalenko KA 2012 Oxidizing and sorptive properties of manganese ore in Siberia Fundamental Problems of Geoenvironment Formation under Industrial Impact: Russian National Conference Proceedings Novosibirsk: IGD SO RAN Vol 1 pp 327–330 (in Russian)
[16] Kovalenko KA 2014 Use potential of manganese ore from Selezenskoe deposit in purification of mining and processing sewage water J. Fundament. Appl. Min. Sci. Vol 1 No 2 pp. 212–216
[17] Bochkarev GR, Pushkareva GI and Kovalenko KA 2010 Arsenic removal from multi-component solutions by sorption Plaksin’s Lectures-2010: Int. Conf. on Science and Modern Integrated Processing of Rebellious Minerals Kazan–Moscow pp 446–449 (in Russian)
[18] Kondratiev SA, Rostovtsev VI, Bochkarev GR, Pushkareva GI and Kovalenko KA 2014 Justification and development of innovative technologies for integrated processing of complex ore and mine waste Journal of Mining Science Vol 50 No 5 pp 959–973
[19] Russian Mining Chemical Company Waste Water Treatment Available at: http://www.magminerals.ru/ application-field/water-treatment-gas-treatment/acidic-waste. Last accessed: 25.04.19