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ARSENIC IN WASTE WATER FROM PRIMARY COPPER PRODUCTION PROCESS

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Abstract

Investigation of arsenic in industrial waste water is of a great importance for environment. Discharge of untreated waste water from a copper production process results in serious pollution of surface water, which directly affects flora and fauna, as well as humans. There is a need for efficient and environmentally acceptable treament of waste waters containing heavy metals and arsenic. The paper presents an analyisis of the waste water from The Copper Smelter which is discharged into the Bor river. The expected arsenic content in treated waste water after using HDS procedure is also presented.
Key words: industrial waste water, arsenic, treatment

Introduction

Industrial development has significantly affected the environment and a change in the social environmental conditions. The outdated copper production technology in Copper mining and smelting complex Bor includes uneconomical consumption of water, a high degree of pollution and a high degree of water stream pollution. Waste industrial water goes into a collector without prior treatment, from where it is sent to the Bor river severely polluting the river itself and affects the quality of the Timok river [1].

Toxisity of arsenic in surface waters [2] is reflected in its effect on the river sediments [3,4] plant and animal world, as well as health of humans [4,5,6]. The U.S. EPA recently decreased the maximum concentration level (MCL) of arsenic in drinking water from 50 to 10 μg/l [7].

A constant increase in production of copper in the world and more strict environmental standards require improvement of the existing and development of new technologies [8,9,10]. This initiated the construction of a New Smelter and Sulphuric Acid Plant in Bor and use of BAT technology [11,12] which also accounts for waste water treatment.

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Material and methods

The Institute of Mining and Metallurgy in Bor tested the waste waters, quantities and content of the effluents that are discharged into the Bor river after accumulation in the industrial collector [13].

Weak acid effluent from the Sulphuric Acid Plant, which is generated during the treatment of off-gases from the Copper Smelter, was sampled once a day, at the facility outlet point, for 11 days in total.

Effluents from the Cooper Electrolytic process was sampled once a day, for 11 days in total, at three measuring points:

1. Measuring point – Cathode Copper Production – Refinery,
2. Measuring point – Copper-Sulphate Production – Regeneration
3. Measuring point – Precious Metals Production – Gold Production Plant

Effluent samples were analysed by using the Atomic Absorption Spectrophotometer Perkin-Elmer's Model 403. This analysis presented current and real concentrations of arsenic in waste waters from the coper production process.

Implementation of new technologies, copper smelting in flash furnace, will result in generation of waste water in the flash furnace gas scrubber, converter gas scrubber and wet electrostatic precipitators in Sulphuric Acid Plant.

Dissolved metal ions will be removed from waste water as a residue in the form of hydroxides. By adding alkali to the solution a new pH value is achieved, metal hydroxsides go into undissloved state and precipitate from the solution. A modified HighDensitySludge (HDS) process will be used for treatment of the waste water from the Copper Smelter Plant and Copper Electrolytic process. This process leads to neutralization of acid and precipitation of heavy metal hydroxides. The process will have two stages, in two reactors, with supplying calcium(II) hydroxide (slaked lime) as a means of deposition. The process consists of the following technological operations [15,16]:

- flow/ quality equalization in a raw waste water storage tank,
- neutralization of acidity using lime and precipitation of calcium(II) sulphate down to its solubility level,
- air oxidation and precipitation of metals as metal hydroxides by sparging air and adding lime to the reaction tanks to elevate the pH to 7.2 in first reactor and to about 9.5 to 10 in second reactor to precipitate metal hydroxides down to their solubility product levels,
- coprecipitation of arsenic with ferric hydroxide,
- deposition in the settler,
- flocculation by adding flocculant to the settler tank, in order to ensure and accelerate deposition of particles,
- discharge of the clarified effluent to a polishing pond before discharging the treated effluent to the receiving stream; the polishing pond has two purposes, one is to achieve quality equalization of the effluent, and the other, to provide a storage reservoar and pump well to house water reuse pumps, as an opportunity for reusing treated waste water
- waste sludge treatment and stabilization

Neutralization of acid, deposition of iron and coprecipitation of arsenic occur in the first reactor with $Fe(OH)_3$ [14,15].

$$H_3AsO_4 + Fe(OH)_3 = FeAsO_4 + 3H_2O \quad (1)$$

In order to ensure deposition of arsenic together with iron, 46.6 %wt Fe2(SO4)3 solution is supplied to the first reactor.

In the second reactor, the achieved pH value is 9.5-10.0 with addition of 13 %wt Ca(OH)2 suspension, which causes full deposition of the remaining iron and other heavy metals. Treated water is discharged into the settler where the solids, consisting of deposited heavy metals in the form of hydroxides, arsenic in the form of iron(III) arsenate and calcium(II) sulphate, generated during neutralization of acid are separated [15,16]. After neutralization and treatment of waste waters in the Effluent Treatment Plant, sludge and treated water are separated.

Results and discussion

Waste water from the Sulphuric Acid Plant occurs as a result of cleaning of the gas generated during the copper production process.

Waste water from Copper Electrolytic Refinery is generated in three technological units: production of cathodes, production of copper sulphate and production of precious metals.

Figures 1,2 and 3 present concentrations of As and quantities of weak acid effluents and electrolytic process effluents which are discharged into the industrial collector with no prior treatment.

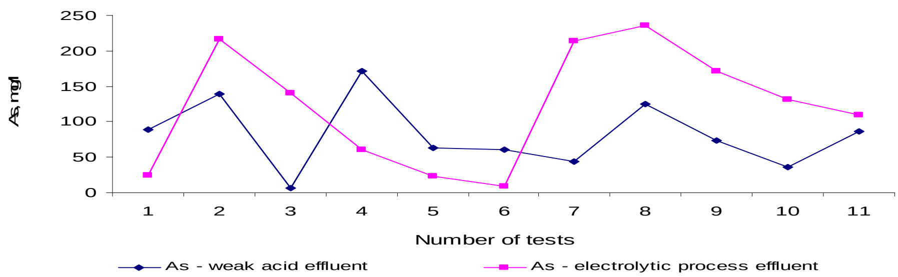

Fig. 1. Concentration of As in weak acid effluent and electrolytic process effluents

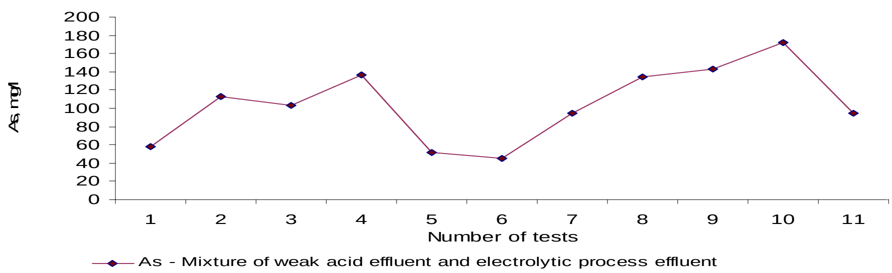

Fig. 2. Concentration of As in the mixture of weak acid effluent and electrolytic process effluents

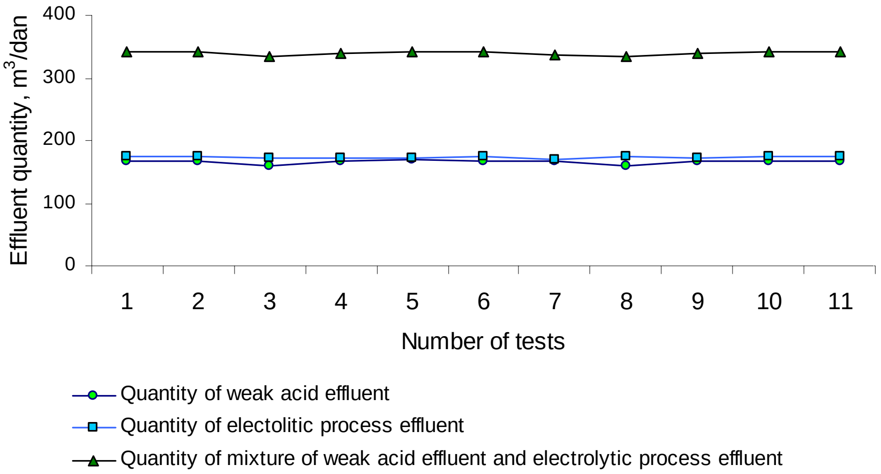

Fig. 3. Weak acid effluent and electrolytic process effluents content at the facility's outlet

Table 1 presents average arsenic content in the Smelter Combine waste waters.

Table 1. Smelter Combine waste waters [13]

Type	Quantity, m^3/h	Average content of As in waste water, g/l	Final inflow
Sulphuric Acid Plant wast water	6.857	0.081	The Bor river
Copper Electrolytic Refinery waste water			
• Copper Electrolytic Refinery	3.125	0.013	The Bor river
• Electrolytic regeneration	2.250	0.280	The Bor river
• Gold Production Plant	2.083	0.028	The Bor river

Under the New Smelter and Sulphuric Acid Plant Project in Bor, SNC-Lavalin and Outotec provided the waste water quality for weak acid effluent (SNC-Lavalin 2012).

Table 2. Weak Acid Effluent Tretment Plant – waste water characteristics [16]

Type	Quantity, m^3/h	Average content of As in waste water (Waste Water Plant inlet), g/l
Flash furnace gas scruber and converter gas scruber	8.66	1.467
Copper Electrolytic process waste water	7.45	0.1

Table 3. Expected arsenic content after treatment in the Effluent Treatment Plant [15,16,17,18,19]

Type	Unit	Expected As content	Republic of Serbia regulations, GVE	EU regulations, parameter limit	EU Tolerance limit
Treated outlet water	mg/l	<0.1	0.01	0.01	0.015

Conclusion

Based on the available data, it can be concluded that waste water treatment is conducted in the manner that is not in accordance with the standards of the Republic of Serbia. For this reason, treatment of this water needs to be done in a separate facility which will be constructed within the New Smelter and Sulphuric Acid Plant Project. Even after the treatment in the Waste Waster Effluent Treatment Plant, the quality of water does not comply with the surface water discharge criteria. Arsenic in treated water requires additional treatment so that the water treated in that manner could be discharged into a recipient.

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