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Impacts of Arsine in Environment and Health of Employees during the Recovery of Metals from Zinc Sulphate Solutions in Trepça

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Abstract: Environmental pollution is one of the most crucial issues of concern in all life fields and is highly required to pay more attention to it in order to protect environment and human been. Environmentally responsible and rentable metallurgical industries put among their key objectives the development of utilization schemes of all of its by-products. The recovery of metals by separation and cementation in metallic forms is overviewed based on the fact that these metals have higher electro-chemical potentials than zinc. Besides zinc, these sulphate solutions contain impurities such as Cu, Cd, Co, Ni, As, Ge, Sb, Se, Te and Ag. Based on the above data, it is evident that the selective recovery of these metals from these solutions represent a significant economic added value, but as well it must take into consideration and arsine as by-product of this process that can be benefit and its effect in environment and employees' health. In this point of view, in order to revive and improve operation practices as per design capacity in the company is necessary to improve the process condition and to avoid the releasing of the arsine in air.

Keywords: *Industry, environment, health, metals, solution, arsine,*

Introduction

According the data from previous years of the Trepca company, and based in design capacity, can produce about 90,000 t/year zinc sulphate solutions as a by-product of neutral leaching of zinc calcine. After the technological process of zinc concentration, calcining and leaching process of Zn, is achieved to be obtained the solution of zinc sulphate. This solution except zinc, contain impurities of different metals such as Cu, Cd, Co, Ni, As, Ge, Sb, Se, Te and Ag. These metal impurities must be substantially removed through succeeding solution purification. Based on the above data, it is evident that the selective recoveries of these metals from these solutions represent a significant economic added value, but in the same time is very important to be careful with the arsenic because of the arsine gas formation. The metal impurities of these solutions may be recovered based on the fact that they have higher electro - chemical potential than zinc and, as such, during the refining process they separate and precipitate in metallic form. Recovery of these metals is important not only by the technological point of view, because in same time it will affect the efficiency of the subsequent step of the electrolysis process, but as well is very necessary to challenge with it as an environmental issue.

The additional processes are needed to take steps to avoid the releasing of the arsine in environment but as well are necessary to protect and employee health which are exposed to him. That show the immediate taking the steps of use of the proper measures and to find the right way to avoid the risk of land filling with it. The improvement of working condition of this process through the proper control of all stages will be subject of this paper.

Cementation process

Impurities in the zinc sulphate are depending on their concentration and properties, and therefore the various chemical and electrochemical refining methods can be used for their recuperation. One of the most known methods which is used in practise is the precipitation or cementation process in which metals of different electrochemical potential are separated by cementation (Kazanbaev, *et al.,* 2006), (D. D. Rodier,1980). In this process electrons are transferred from zinc to other metals, a process that can be expressed by the following general chemical reaction (Krüger, *et.al*.,2001))

$$Me^{n+} + n/2\ Zn \rightarrow n/2\ Zn^{2+} + Me \qquad \text{(Eq. 1)}$$

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where: Me = Fe, Al, As, Sb, Ge, In, Ga, Si, Cu, Cd, Co, Ni, Ta, Cl, Fl, K, Na, Mg, Mn, and "n" is the valence.

Cementation takes place because zinc has a more positive oxidation potential than the impurities. Impurities in the zinc solutions, depending on their concentration and some common properties during the separation process, can be classified into the following groups:

1. Fe, Al, As, Sb, Ge, In, Ga, Si
2. Cu, Cd, Co, Ni, Ta
3. Cl, Fl,
4. K, Na , Mg, Mn

The zinc sulphate solution is considered to have a high refined degree if it is a very clear solution and has the following characteristics: solid substances <0.5 g / l, Fe2+ <5 mg / l, total Fe <15 mg / l, Sb + As <1 mg / l and pH = 5 - 5.5. (Purification process,1982)

Methods for the zinc solution purification

The usually methods for the zinc solution purification are the "hot-cold" and the "reversed" purification processes. In both methods the liquor is purified by cementation of harmful elements with zinc dust and activators in a continuous, multistage process. The disadvantages of these procedures are the high zinc dust consumption and even more the complex composition of the residues.

The process of refining of sulphate solutions and recovering of valuable materials from it is a complex process whose normal running and its efficiency depends on numerous process parameters. These parameters in the Trepca process include the content of solid substances, $Fe^{2+,}$ Fe total and Sb + As concentration of, pH of solution, added amount and the size of particles of zinc powder during cold and hot refining, processing time and temperature, the speed of filtration, lead quantity, mixing with the electrolyte. (Purification process,1982)

The purpose of the refining process of solution is maximally removing of the impurities from zinc sulphate solutions and produces a highly refined solution, and therefore is applied two stages of refining:

- Cold refining
- Hot refining

Description of arsine gas

Arsine (AsH3) (CAS No 7784-42-1) does not occur in the natural environment and first was obtained by Scheele in 1775. Arsine is an inorganic compound and simpler compounds of arsenic. Is known as a colourless, flammable, highly poisonous, nonirritating, and highly toxic gas. It has a garlic-like or fishy odour that can be detected at concentrations of 0.5 ppm and above. Arsine is water soluble. Exposure may occur when arsine gas is generated while metals or crude ores containing arsenic impurities are treated with acid (URL-3). Reaction of arsenic-containing substances with newly formed hydrogen in water or acids leads to formation of arsine gas.

The impact of the arsine gas released into the environment and health of employees

In this paper will examine and consider case of the arsine, during the above-mentioned processes and his impact in environment and health of employees. It is now produced commercially, and either by the metallurgical processes. Exposure to levels below the odour threshold may present a health hazard. If water or acid contacts ores or metals that contain arsenic, they may release arsine gas at hazardous levels. Substances that occur as the most frequent pollutants of arsine are ores that contain arsenic. For this reason, it must to be carefully with them, because they may release arsine gas at hazardous levels. Specific matter of air pollution can be created if water or acid contacts ores or metals that contain arsenic.

Although in some countries in which industry is more developed, are taking concrete steps towards environmental protection through the application of legislation which defines the amount of each pollutant that is allowed to be emitted into the atmosphere. In countries that are in the development phase, still are in use outdated technologies and as a result of this we face greater pollution of the environment. In most of cases, particularly in the chemical and metallurgical industries source of exposure to arsine in workplace is very real, because of poisoning with arsine have been associated with the use of acids and crude metals, which contained arsenic in a form of impurity.

During the abovementioned processes, there is real possibility to have releasing of the arsine gas due to its accidental formation as a by-product, and therefore is necessary in advance to be prepared to be protected by it. Exposure to arsine majorly occurs through inhalation. It is non-irritating and creates no urgent warning signs. Symptoms like nausea, dizziness and abdominal pain may be experienced within few hours of contact with 3 ppm of arsine. Exposure to large dose of arsine may lead to additional health implications including convulsions, paralysis, and respiratory failure. Skin contact with liquid arsine can lead to frostbite. Severe exposure to arsine is fatal in most cases (URL1).

Treatment from Arsine Exposure

In this section are given some details related the guidelines for protection in work during the processes described above. During the work for zinc benefit we must to take care from arsine gas, which can be gained as secondary product. Because arsine is noirritating and produces no immediate symptoms, persons exposed to hazardous levels may be unaware of its presence. (URL-2), and therefore is part of each company to check:

1. The functionality of the ventilators;
2. The reactor caps (must be closed);
3. Cleaning of the reactors is allowed to start after one hour of ventilation;
4. The worker, before entering the reactor to clean it, must have the work clothes and the inductive letter. This letter is used 1m above the end of the reactor;
5. Mask (respirator) for arsine protection(AsH3) should be used;
6. Workers working in the cleaning section should always have an indicative letter of protection for arsine(AsH3) with them;
7. Explosion hazard (H2), when working on a reactor with a tin smelter;
8. Never do the cleaning of the accumulating manholes with the electrolyte from the cells;
9. Always use wood tools (not metal);

To beware of the possibility of forming AsH_3:

1. $M(Zn) + H_2SO_4 \rightarrow ZnSO_4 + H_2$ M – metal (Eq. 2)
2. $3/2H_2 + As \rightarrow AsH_3$ (Eq. 3)
3. $3Zn + 6H_2O \rightarrow 3Zn(OH)_2 + 3H_2$ (Eq. 4)
4. $3/2H_2 + As \rightarrow AsH_3$ (Eq. 5)

We can withstand: 1 hour at 1 ppm, and rapid death occurs when the concentration is 100 ppm (400mg/m^3). The indicative letter changes the colour to 5 - 20 ppm. These observations remarks apply to all workers working in the cold, hot, and Cu / Cd and Co / Ni repulse section. The indicative letter changes the colour to 5 - 20 ppm. If the indicative letter changes the colour, the employee must immediately leave the site and notify the responsible engineer (Purification Process, 1982).

Summary of Health and environmental effects of arsine

The toxicity of arsine is distinct from that of other arsenic compounds. The main route of exposure is by inhalation, although poisoning after skin contact has also been described. Arsine attacks hemoglobin in the red blood cells, causing them to be destroyed by the body. The first signs of exposure, which can take several hours to become apparent, are headaches, vertigo and nausea, followed by the symptoms of hemolytic anemia (Holleman *et.al*., 2001).

It is classified as an extremely hazardous substance in the United States as defined in Section 302 of the U.S. Emergency Planning and Community Right-to-Know Act (42 U.S.C. 11002), and is subject to strict reporting requirements by facilities which produce, store, or use it in significant quantities (C.F.R.2008).

All arsenic compounds are toxic; arsine is particularly toxic because of its gaseous nature. It has a strong garlic odour. This gas is formed whenever hydrogen is produced in presence of arsenic-bearing solutions. Traces of arsenic in scrap, in ores, and in metallurgical residues find their way as arsine under certain conditions in Table 1 (Habashi, 2011).

Table 1. Pollution problems in the metallurgical industry from arsine. Threshold limit values of toxic gases found in metallurgical plants in decreasing order of toxicity

Gas	Formula	Threshold limit value in air		Remarks
		ppm	mg/m^3	
Arsine	AsH_3	0.05	0.2	Toxic

Conclusion

Arsenic is an element that raises much concern from the both environmental and human health standpoints. Occupational and environmental health problems can result from the frequent commercial presence of arsenicals. Exposure to arsine gas is also an environmental health hazard of concern in numerous occupational circumstances. Controlling of the arsine gas releasing in air and its effects in employee health is the main aim of this paper, which is not easy to be controlled and therefore explain the fact has faced with the difficulty in the industrial practice. This review details the known health effects of arsine as well as the existing theories on the mechanism by which arsine exerts its toxic effect and conditions of occupational exposure to this gas. Exposure to arsine in occupational settings occurs mostly in the chemical and metallurgical industries when nascent hydrogen reacts with metallic arsenic or arsenic compounds. The available data indicate that in these branches of industry arsine is often a cause of unexpected serious poisoning. The gas affects primarily blood and kidneys.

The toxicity of the gas brings about the increased osmotic fragility of red blood cells, formation of erythrocyte debris in capillaries and effects on hemopoietic tissue. The current occupational exposure limits in the majority of countries prevent the hemolytic effects of the gas. Meantime, the gas should be handled with proper care. In general, a little attention has been given to arsine despite its extensive use and the risk of its unintended formation during many chemical and metallurgical processes.

It was also evidenced that this process of sulphate purification is dependant of process parameters that need to be controlled carefully, because of their impact to the environment, especially of arsine gas. A proper control and automation technique in purification stages for this refining process of zinc sulphate solution, offers also the opportunity to makes possible a successful and efficient application of this technology in the industrial practice. This includes several parameters such are quality of solution, adding of reagents, the speed, duration and temperature of the process. The benefits of this application results with positive outcomes in the intensification of technological processes, minimization of reagent consumption, increase of production capacity and quality, which directly reflected in environment and health of employees (Nelson *et.al*, 2000).

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