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ARSENIC IN THE COOPER'S MINERALS: AN OPTION FROM THE PIROMETALURGY

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Abstract

The purpose of this paper presented at RECI-MAT-09 is to address, briefly and as clearly as possible, expectations which may have arisen from the basic and applied research regarding the increasing problem of pollution caused by arsenic derived from copper metallurgy.

In addition to the metallurgical problem which has not been resolved on an industrial scale, there are difficulties with the environment, with energy variables (both exothermic and endothermic reactions) and materials or by-products related to nanoscience and nanotechnology. This type of product may originate from the emergence of new solid phases due to condensation vapour.

Finally, since large amounts of high quality As_2O_3 metal are being produced naturally through this process, this would be a good time to look at the situation as a real opportunity rather than a problem that must be avoided. We need think only about what it would mean to lower costs and thus prices in the electrical industry - electronic: semiconductor and photovoltaic solar energy, mass and the economic feasibility of the chalcogens (chemical combinations between elements of the III and VI columns in the Periodic Chart) [1].

Keywords: Pollution, arsenic, copper metallurgy, nanotechnology, solar & nuclear energy

INTRODUCTION

The presence of arsenic in traditional copper ores occurs either in the form of enargite, Cu_3AsS_4 , or arsenopyrite, $FeAsS$.

The presence of arsenic in the mineral (all-one, 0,50-1,00% Cu) and in the subsequent copper concentrates (25 % CU) that arrive at the foundry is a well known problem in copper metallurgy

[2]. To bring us inside the industrial context and weigh possible solutions, it is necessary to bear in mind the following:

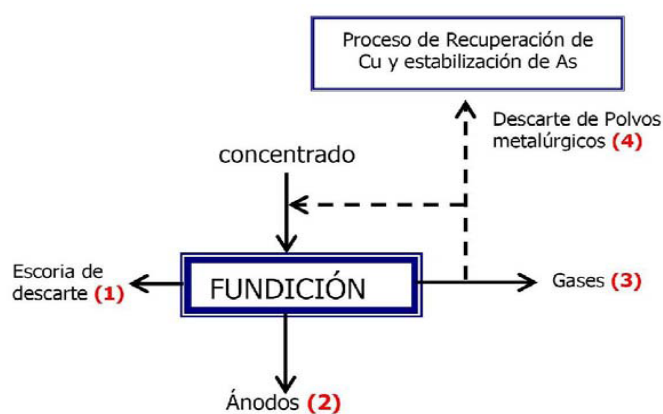


Figure 1. Distribution of minor elements in a Cu smelter operation

1. Around 80 % of primary copper production comes from the pyrometallurgy method. Therefore, a solution to the problem of arsenic affinity would be one which would result in the arrival at the refining or converter furnaces an arsenic-free raw product which conforms to the specifications of raw materials fed into the process. In short, develop an arsenic-removal system compatible with current foundry infrastructure.
2. One of the first extraction operations is a concentration-fusion process which results in a mixture of melted copper sulphides and iron known as "copper rust" which reaches an average concentration of 60% Cu (mineral content of copper presented in the environment is between 0.50 and 1.00% while its concentrates reach up to 25% CU). During this operation, most of the arsenic that was present

in the ore is eliminated and collected with the rest of the volatile material in the bag filters present in foundry installations (Figure 1).

- Copper is the non-ferrous metal second in importance due to its demand - consumption. Figure 2 shows the evolution of the production of copper in recent times. Within the European Union, the most important primary copper-producing countries are: Germany (650,000 tonnes/year), Poland (500,000 t./year) and Spain (400,000 t./year).

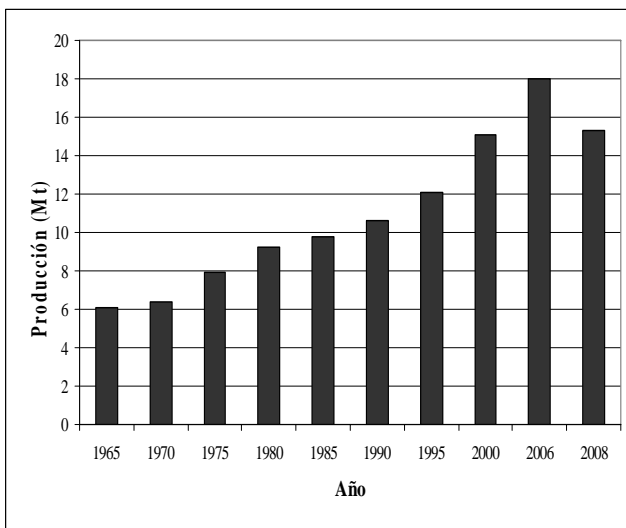


Figure 2: World Copper Production (million tonnes)

PROPOSAL TO RESOLVE THE PROBLEM

Considering that currently there is no industrial process capable of dealing with copper concentrates with high arsenic content ($\%As \geq 1\%$). At the laboratory scale, the high-efficiency roasting process, which removes volatile substances using temperatures of approximately $750\text{ }^{\circ}\text{C}$, is used to reduce to the component parts volatile polymetallic sulphides which were present in the copper. The rest of the impurities (copper and iron sulphides) remain without reacting due to the existence of a potential oxygen system (partial pressure or concentration of gaseous oxygen). Thus iron and copper sulphide oxidation plays only a very small part in this process. However, as the process is heat self-sufficient, some amount of iron sulphides do mostly oxidize. The energy input necessary to maintain the temperature of the roasting – volatilization of concentrates with a high arsenic content is associated with iron oxidation.

Due to the requirements of the fusion for copper rust furnaces, though, the magnetite content in the final product cannot exceed $4\% \text{ Fe}_3\text{O}_4$ (Figure 3) [3].

At the scale of laboratory reactors (25.0 cm in diameter), volatile gases of arsenic sulphide quite efficiently separate from copper concentrate, resulting in a product with less than $0,1\%$ arsenic.

The volatile gases from the roasting process - contain in addition to arsenic sulphides, As_2S_3 , anhydric sulphur dioxide, SO_2 . Before fixing or extracting the SO_2 as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or as sulphuric acid, H_2SO_4 , it would be advisable to eliminate the arsenic it may carry.

Through a suitable gas-solid reactor, the oxidation of arsenic sulphide gases (an exothermic reaction) can be induced which would lead to the precipitation of arsenic trioxide, As_2O_3 (a white powder).

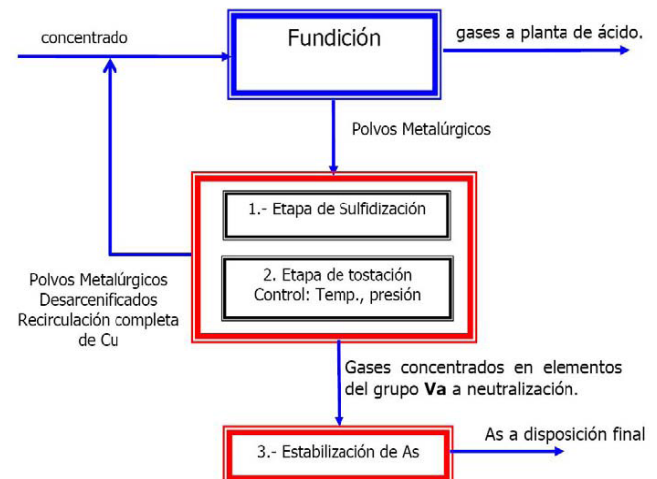


Figure 3. Flowchart for the non-oxidizing roasting process proposed to remove arsenic from concentrates and powder copper metallurgy

The properties of arsenic trioxide may be decisive in the later creation of a by-product. The intervention of the mechanisms of nucleation and growth can lead to a variety of physical and chemical qualities which need to be further studied: powders with nanotechnology characteristics may be obtained.

Key points in the success of the process is the control of temperature and oxygen potential associated with the decomposition system – arsenic volatilization.

MANAGEMENT OF OBTAINED BYPRODUCTS

Perhaps one of the greatest difficulties for the development of arsenic-related technologies is due to the fact that its mere presence creates an environment "*social alarm*". The usage of products such as arsenic trioxide, however, does not reveal significant complications due to its high chemical stability, although its presence as an aerosol in the air in significant proportions is particularly harmful to ones health.

Nevertheless, their important applications in the semiconductor industry and in particular for the manufacture of compounds such as gallium arsenide, GaAs, and indium arsenide, InAs, indispensable in the military industry, has forced its presence onto the market [4].

The energy crisis which has been caused by an excessive dependence on oil, has forced the Western world to orient its strategies towards other sources of energy. Among these, we have both nuclear energy as well as solar power.

The main objection imposed on nuclear energy is the need for the efficient management of waste. To date, a consensus has been reached by which the most environmentally respectful way of doing this is the encapsulation of the radioactive waste within a glass-like structure.

If the market is able to have at its disposal an abundant and economic source of arsenic (thousands of tons/year) as a result of the massive use of concentrated copper high arsenic, the As_2O_3 in such circumstances, rather than an inconvenient and annoying waste, would turn out to be a "good opportunity" to:

- a) Make the production of GaAs and InAs available at low costs for mass production of solar panels [4].
- b) Use the rest of arsenic to collaborate in order to "inertize" the radioactive waste under the shape of arsenical glass.

The solar photovoltaic literature highlights the high cost of the substrates in the development of the GaAs as a major drawback (or other combinations of Group III As elements: In; Al or or Ti). For this reason the use of these cells is currently limited to the so-called photovoltaic concentration systems: to obtain high efficiencies (30%) with a small size exposure area (0.25 cm²).

CONCLUSIONS

Through out the text of this paper we have particularly wanted to highlight the multidisciplinary nature of the "Arsenic Problem in Copper Metallurgy". In addition to resolving and demonstrating the significant metallurgical challenges at the industrial level, it proposes problems related to energy efficiency, the environmental and management, - management and use of small size (nanotechnology) products.

The mass production of elements traditionally considered as dangerous to the environment, may constitute a good opportunity for solar energy or as nuclear power, when trying to favorably solve the problems of efficiency and waste that can either slow down or limit their development.

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