



Study of toxicity of arsenic during the synthesis of new class of iron-based oxyarsenide superconductors

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Abstract The toxicity of arsenic and its severe effect on human-beings are reported in this study. The different exposure limits of various materials are described during the synthesis of iron-based superconductor as a time-weighted average (TWA) over an 8-hours workday. This report reveals that the element arsenic is found to be highly toxic in case of inhalation or ingestion by the employers amongst the starting materials during the synthesis of oxyarsenide superconductor. All the exposure limits are taken from Occupational Safety and Health Administration (OSHA) regulations. This study helps to increase the primary care provider's knowledge of hazardous substances such as arsenic in the environment and to promote the adoption of medical practices that aid in the evaluation and care of potentially exposed patients.

Keywords Iron-based superconductor; toxicity; arsenic, exposure limits, extracted

Introduction

The recent discovery on the new class of iron-based superconductor has broken the tyranny of copper. The innovation of 26 K transition temperature (T_c) in fluorine-doped LaFeAsO superconductor [1] marked the beginning of worldwide efforts to investigate this new family of superconductors. After several efforts the T_c has reached 55 K by replacement of Lanthanum (La) by other rare earth elements [2-4]. This new class of superconductor involves a complex chemistry in the synthesis, on the contrary to cuprate-based superconductor. Despite of complex structure, some scientists would not want to work with this new superconductor due to toxicity and volatile nature of arsenic element. In March 2008, at the Argonne National Laboratory in Illinois, an encapsulated tube of arsenic exploded when researchers were synthesizing the new material for the first time [5-7]. This issue has raised the questions over this new family of superconductor. Therefore, prior precautions are needed during the synthesis for this new group of sample.

In this report, we will discuss the adverse effect of the arsenic on human being and its safe handling during the synthesis of oxyarsenide superconductor.

Results and Discussion

Effects of arsenic toxicity on humans

Table 1 shows the exposure limits for various materials used in the synthesis of iron-based new class of high T_c superconductor. The reference contamination, in mass per unit volume of air, resulting from processing depends on the volatility of materials as well as on precautions taken to isolate the process. The volatile oxides have comparatively low melting points. In case of high critical current applications, hazards sometimes include the possibility of device overheating after quenching of superconductors. In general, exposure limits are reported in parts per million (ppm), or milligrams per cubic meter (mg/m^3). However, substances present in air are as a form



of vapour and aerosol which are typically reported in ppm and mg/m^3 , respectively. Natural arsenic is made of one isotope ^{75}As .

Table 1: Exposure limits for starting materials used during the synthesis of new class of oxyarsenide superconductor, $\text{SmFeAsO}_{1-x}\text{F}_x$

Starting materials	Toxicity/ reactivity/damage	Permissible exposure limits in air (8-h TWA) (mg/m^3)	Melting point ($^{\circ}\text{C}$)
SmF_3	low toxicity by skin absorption, inhalation of dust may cause lung damage	2.5 [8]	2383
Sm	slightly toxic	N.A.	1074
Fe	poison by ingestion; chemically very reactive, and rapidly corrodes	N.A.	1538
Fe_2O_3	repeated exposure of fume can cause siderosis with cough, shortness of breath	10 [9]	1565
As	highly toxic; poison by inhalation, ingestion and skin contact	0.01 [10]	614

Values of refs. [8], [9] and [10] have been taken into account from OSHA (Occupational Safety and Health Administration) regulations.

Elemental arsenic (As) have two solid forms: yellow and gray, with specific gravities of 1.97 and 5.73, respectively. Gray arsenic, the ordinary stable form, has a triple point of 817°C and sublimates at 614°C and has a T_c of 1400°C . Several other allotropic forms of arsenic are reported in the literature. It tarnishes in air, and when continuously heated, rapidly oxidized to arsenous oxide (As_2O_3) with the odor of garlic. Arsenic and its compounds are poisonous. Exposure to arsenic and its compounds should not exceed 0.2 mg/m^3 during an 8-h work day. Arsenic is commercially available in high-purity form. The usage of As is increasing as a doping agent in solid-state devices such as transistors. Gallium arsenide is used as a laser material to directly convert electricity into coherent light.

Hydrogen gas can react with elemental As to form arsine. The As is flammable in powder form or by chemical reaction with powerful oxidizers viz bromates, chlorates, iodates, and peroxides. Arsenic is reacted with other elements such as, oxygen, chlorine, and sulfur to form inorganic arsenic compounds. Therefore, care should be taken to synthesize the iron-based oxyarsenide superconductor where As is one of the starting material.

Inhalation, ingestion, or skin contact of employers to inorganic As has caused peripheral nerve inflammation (neuritis) and degeneration (neuropathy), reduced peripheral circulation, anemia, enhanced mortality due to heart failure, and cancers of the lungs, skin, and lymphatic system. The short-term exposure to inorganic As can cause nausea, vomiting, diarrhea, weakness, skin and eye irritation, cough, chest pain, giddiness, headache, and respiration problem (dyspnea).

It is advisable that chemical protective clothing (CPC) should be use throughout the synthesis of As doped superconductor. Employers should be provide the other appropriate protective clothing, spectacles, and gloves necessary to prevent skin contact during the preparation of this kind of superconductors. By the way, if something explodes, contaminated clothing should be removed immediately and keep in dustbin especially designed for hazardous materials for the safe disposal.

At the time of explosion, if the As gets into eyes, flush the water into eyes for 15 minutes from the eyewash fountain and consult with the medical practitioner at an earliest. If there is any possibility of an employer's body being exposed to elemental arsenic, facilities for quick dressing of the body should be provided at emergency level.

During the synthesis of As doped superconductor, if encapsulated tube explodes, the following steps should be taken immediately: (1) remove all the ignition sources around the accident area, (2) open all windows and ventilate that area, (3) don't use the vacuum cleaner to remove the contaminated dust of As doped superconductor, (4) use proper mask, gloves, goggles, and CPC during the cleaning and dispose these things after the usage.



It must be noted that the use of respirators is the unusual method of controlling employer exposure and should be used when work practice controls are not technically feasible, or at the meantime of emergencies. Air purifying respirators must be avoided because these respirators will not protect from oxygen-deficient environments.

Calculation of air As inhalation doses for the normal person, adult inhalation exposure dose in mg/day can be described as:

$$I_{ED} = \frac{C \times I_R \times E_F}{B_W}$$

where,

C = contaminant concentration = 0.00060 mg/m³ (say)

I_R = inhalation rate (20 m³/day)

E_F = exposure factor (unitless)

B_W = body weight (let 70 kg for adult person)

$$I_{ED} = \frac{0.00060 \times 20 \times 1}{70} = 0.00017 \text{ mg/day}^*$$

Cancer risk can be calculated as:

Inhalation Unit Risk = 0.0045 (μg/m³)⁻¹ (say)

Risk = Inhalation Unit Risk x Concentration

= 0.0045 x 0.60

= 0.0027*

*These calculations are based on the assumptions for the worst case situation; the actual values of exposure would be less.

The damage of lung cancer and bronchitis occurs in human when the arsenic is inhaled through the respiratory system [6]. In 1836, James M. Marsh developed a technique for the existence of As in tissue. Three years later, Orfila successfully extracted the As from the human tissues followed the Marsh's technique. In 1889, Ernst Wilhelm Heinrich Gutzeit discovered a procedure to count the concentration of As in tissues. In this process, As compounds are reduced by hydrogen when zinc and sulfuric acid react. The hydrogen then reduces the As compounds to arsine, which is kept on paper to treat with mercuric chloride solution. This gives a color range from yellow to brown as per the As concentration [7].

Conclusion

Enormous exposure limits are mentioned for starting material involves during the synthesis of new class of iron-based superconductor, SmFeAsO_{1-x}F_x. The least exposure limit of element arsenic is found to be highly toxic over an 8-hours work shift. In order to avoid the bundle of diseases; mask, gloves, goggles and CPC should be used throughout the synthesis of this type of superconductors. Briefly, the safe handlings of arsenic are discussed in this paper.

References

1. Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. (2008). Iron-Based Layered Superconductor La[O_{1-x}F_x]FeAs (x = 0.05-0.12) with T_c = 26 K. *J. Am. Chem. Soc.*, 130:3296.
2. Chen, X. H., Wu, T., Wu, G., Liu, R. H., Chen, H., and Fang, D. F. (2008). Superconductivity at 43 K in SmFeAsO_{1-x}F_x. *Nature*, 453: 761
3. Ren, Z.A., Yang, J., Lu, W., Yi, W., Shen, X.L., Li, Z.C., Che, G.-C., Dong, X.L., Sun, L.-L., Zhou, F., and Zhao, Z.-X. Superconductivity in the iron-based F-doped layered quaternary compound Nd[O_{1-x}F_x]FeAs. (2008). *Europhys. Lett.*, 82:57002.
4. Cheng, P., Fang, L., Yang, H., Zhu, X., Mu, G., Luo, H., Wang, Z., and Wen, H.H. (2008). Superconductivity at 36 K in gadolinium-arsenide oxides GdO_{1-x}F_xFeAs. *Sci. Chin.*, G 51:719.
5. Eric, H. (2008). Arsenic heats up iron superconductors, *Nature*, 452: 922.



6. *A Textbook of Modern Toxicology, Third Edition*, edited by Ernest Hodgson ISBN 0-471-26508-X (2004) John Wiley & Sons, Inc. pp 318
7. *A Textbook of Modern Toxicology, Third Edition*, edited by Ernest Hodgson ISBN 0-471-26508-X (2004) John Wiley & Sons, Inc. pp 399
8. http://www.lookchem.com/msds/26534/13765-24-7_Samarium-fluoride-SmF3-.html
9. <http://www.osha.gov/chemicaldata/chemResult.html?RecNo=206>
10. <http://www.osha.gov/chemicaldata/chemResult.html?RecNo=528>

