

REMOVAL OF REFRACTORY LININGS IN ALUMINUM MELTING
AND HOLDING FURNACES

1. SCOPE

This standard covers precautions necessary when removing the refractory lining materials from melting and holding furnaces. The precautions cover a) Phosphate bonded refractory materials and b) Asbestos containing refractory materials. Portions of this standard are taken from OSHA 1910.1001 and the ~~Alcoa Association Industrial Hygiene Code~~.

2. PHOSPHATE BONDED REFRACTORY

2.1 General. There have been several ~~reported~~ incidents wherein Alcoa employees engaged in dismantling furnaces have been exposed to phosphine. These exposures have been associated with the use of phosphate-bonded alumina refractories, and in particular UV-38 brick and Ramtite's 90 Ram Fine. Although other phosphate-bonded alumina refractories in use in our plants such as H. K. Porter's Multex-75, General Refractories Altex-55, North American's Nardal B5-B, and France's Spartan-B5 have not shown any evidence of gas evolution, the potential remains. Phosphate bonded refractory material is commonly found in melting and holding furnaces and ladles. The phosphine problem was first brought to our attention during the repair of a UV-38 hearth that had failed prematurely. In order to minimize the dust generation that accompanies dismantling work and to expedite the disintegration of the reacted brick, the workers wet down the floor of the furnace. Their use of the jackhammers brought unexpected results. Striking the UV-38 hearth with a jackhammer produced minor firecracker-like explosions. Small match-like flames continued to burn in the area where the explosions had occurred. Although an odor was noted, it was interpreted as being the usual acetylene-type that is noted frequently during brick removal. Subsequently, similar incidents were reported. Because the generated gases were spontaneously flammable, phosphine was suspected early, and it eventually was positively identified.

Pyrotechnics have also been reported during the removal of brick that contains no phosphate. Therefore, the presence of fireworks is not positive proof of the presence of phosphine. On the other hand, if explosions and flaming occur, the work's industrial hygienist, with the aid of a detector tube, should determine whether or not phosphine is present.

2.2 Removal of Refractory. The removal of phosphate-bonded refractory materials should be done in the dry condition, because this method is usually a very dusty one, the use of respiratory protection is recommended. Respirators fitted with filters suitable for removing nuisance dusts will be satisfactory. The respirators should be

equipped with valves so that, on exhalation, moist breath does not contact the dust collected on the filters.

If for some reason one of these furnaces is wetted down, it will be necessary for the works industrial hygienist to sample the working area to insure that there are no hazardous concentrations of phosphine. Man-coolers or other ventilation assists may be useful in clearing out any contaminated area. If there is any need for a person to enter a contaminated area (i.e., where the PH_3 concentration is above the 0.3 ppm TLV) - he will require personal protection, either a self-contained air unit or an all-service gas mask.

Moisture in the air can release phosphine from stored reacted brick following its removal from a furnace. Therefore it should not be stored in a confined place, especially if employees work in the area. If there are any concerns about the safety of the area it will be a simple matter to sample the air with a detector tube.

Because of the relatively high toxicity of phosphine, we must take a rather conservative position to be assured as completely as possible that our employees are protected. Dismantling of a furnace is an infrequent operation of a relatively short duration. For this reason, chronic exposures just don't exist. Even the probability of acute exposures occurring is limited.

The chemistry of what happens in the brick is still obscure. Water is necessary to release the phosphine from the phosphide in the reacted brick. When wetted, the phosphide-containing brick releases phosphine gradually. Furthermore, the spontaneous ignition that often accompanies the release of phosphine results in the conversion of phosphine to a much less toxic material, phosphorous pentoxide.

However, it must be noted that even the normal humidity of the air is capable of reacting with the phosphides and releasing small amounts of phosphine. The refractory gradually loses its reactivity when it is exposed to air.

A typical analysis of the gases evolved from the wetted reacted brick is 70% H_2 , 20% PH_3 , and 10% other unknown gases (possibly N_2 , O_2 , NH_3 , etc.). Our experience has shown that the analyses may vary widely but the PH_3 concentration is just as likely to be higher than shown above as lower. Therefore, PH_3 will always be the material of prime concern.

The brick that produced the gas above released 0.1 ft³ per square foot of surface over a 24-hour period. By extrapolation we can figure that a 250 ft² hearth would produce 25 ft³ of gas, of which 2.5 ft³ is PH_3 . In order to bring such a quantity of

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Ph₃ down to the Threshold Level Value, 0.3 ppm, it would have to be diluted with 1,000,000 ft³ of air. There are a lot of weaknesses in extrapolating in this manner and the figures should not be taken too literally. However, the inference drawn from this is that we are dealing with appreciable quantities of a toxic gas.

The presence of NH₃ will not cause any appreciable interference for those who have occasion to use the Kitagawa Ph₃ detector tube to measure this gas. Hydrogen sulfide, a gas that will interfere, was not detected in the products given off by the brick. Arsenic and stibine will also interfere but they are not expected to be present. The above can be interpreted to mean that when sampling the gases produced by the reacted brick with a Kitagawa detector tube the length of stain produced on the tube, for all practical purposes, can be attributed to phosphine.

2.3 Phosphine Gas. Phosphine is a colorless gas with an odor described as like that of garlic, decayed fish, or onions. It has an auto-ignition temperature of 104 Deg-105 Deg F (40-65 Deg C), but may ignite at room temperature due to impurities or when dry. The relative density of saturated air at 25 Deg C and 760 mm Hg is 1.17 (air = 1). (Ref. Hazardous Material Safety Data Sheet No. 213).

The mechanism of phosphine intoxication has not been definitely established, but it appears to cause depression of the central nervous system and irritation of the lungs. The symptoms of acute phosphine poisoning reported include nausea, vomiting, diarrhea, thirst, sensation of pressure in the chest, back pains, dyspnea, feeling of coldness, and super or attacks of fainting.

3. ASBESTOS CONTAINING REFRACTORIES

OSHA 1910.1001 states that no employee shall be exposed at any time to airborne concentrations of asbestos fibers in excess of 10 fibers, longer than 5 micrometers, per cubic centimeter of air. The 8 hour time weighted average airborne concentrations of asbestos fibers to which any employee may be exposed shall not exceed 2 fibers, longer than 5 micrometers per cubic centimeter of air. (Reference Hazardous Material Data Sheet #40 for additional information.)

3.2 Removal Procedures. Initial site preparation involves taking precautions to contain entrained asbestos fibers to the immediate work area.

The size of the enclosure must be large enough to contain the power equipment, an approved vacuum cleaner, and several 55 gallon specially marked steel drums.

USHA 1910.1001 states that employees engaged in the removal or demolition of structures or equipment covered or insulated with asbestos, shall be provided with respiratory equipment and with special clothing.

3.2.2 Clothing. The employer shall provide, and require the use of, special clothing, such as coveralls or similar whole body clothing, head coverings, gloves, and foot coverings for any employee exposed to airborne concentrations of asbestos fibers, which exceed the ceiling level prescribed in 3.1.

Disposable coveralls, gloves, hair covering (under the hard hats) and respirators approved for asbestos shall be worn at all times when work is in progress in the enclosure. The coveralls are to be taped at the ankles and wrists. All disposable clothing is to be removed and discarded each time a workman leaves the work area. Shoes must be wiped with a damp rag or vacuumed so that the area outside the enclosure is not contaminated. Before leaving the contaminated area for any reason, the workmen shall vacuum the protective clothing, remove the head covering, unzip the coveralls and carefully peel them off, with gloves and shoe coverings remaining attached. The respirator is removed last. The disposable clothing and used filter cartridges shall be disposed of in plastic bags, appropriately labeled for asbestos waste. Respirators shall be cleaned and sanitized at the end of every shift. Workers must wash all skin surfaces that have been exposed to asbestos before eating, drinking, smoking or leaving work. Any water that is used for these purposes must be placed in plastic bags and then into the drums with the contaminated clothing. No smoking or eating is permitted while in the enclosure.

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Caution signs shall be provided and displayed at each location where airborne concentrations of asbestos fibers may be in excess of exposure limits prescribed in 3.1. *add info*

sealed steel drums shall be affixed with labels that read:

CAUTION
CONTAINS ASBESTOS FIBERS
BREATHING ASBESTOS DUST MAY CAUSE
SERIOUS BODILY HARM

These drums must then be disposed of in an approved land fill. Most land fill facilities cannot accept this kind of waste so there is an incentive to completely fill the drums.

3.4 Outside Contractors. It is imperative that the outside contractor know he is dealing with asbestos. It is recommended that a copy of Alcoa Material Safety Data Sheet No. 40 (asbestos) be included with either the specifications or the order, as well as verbally calling the contractor's attention to the hazard.

Alcoa has no direct liability under the asbestos section of OSHA 1910.1001 for the contractor employees while the contractor is demolishing the furnace. The contractor should be required to furnish approved respiratory equipment and special clothing for his employees as noted in OSHA 1910.1001(c)(2)(iii).

The final cleanup of pieces and particles that may contain asbestos fibers shall be bagged and sealed in specially marked steel drums (see 3.3) and labeled according to OSHA 1910.1001(c)(2)(ii). Final disposition of the material shall be as covered by RCRA.

The disposal of all asbestos containing waste material as well as contaminated material requires special procedures. Asbestos containing insulation, contaminated refractory rubble, the used disposable clothing, loose material picked up with the vacuum cleaner, wiping rags, rinse water from the wiping tank, and finally the plastic enclosure sheeting shall be packaged in plastic bags and then sealed in specially marked steel drums. OSHA states that caution labels shall be affixed to all scrap, waste, debris, and other products containing asbestos, or to their containers. All plastic bags and

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