Health Hazard and Pollution in the Metallurgical Industry Due to Phosphine and Arsine

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Abstract

Health hazards and pollution due to the formation of PH₃ and AsH₃ are reviewed. These poisonous gases are formed during the following metallurgical operations:

1. dissolution of a metal containing traces of P and As in acid, e.g., cementation of Cu by Fe, Cd by Zn, etc.;
2. dissolution of an As-free metal or oxide in an acid containing As, e.g., leaching of Zn or ZnO in dilute H₂SO₄;
3. reaction of ferroalloy or an intermetallic compound containing traces of P or As with moisture in the air or water, e.g., FeSi, FeMn, alloys and species;
4. decomposition of carbides containing traces of P by reaction with water, e.g., CaC₂;
5. electrolysis of a solution containing traces of As, e.g., during electrolysis of CuSO₄ or ZnSO₄, solutions for Cu and Zn recovery.

Introduction

PHOSPHINE AND ARSINE are two highly toxic gases (Table 1) that are formed quite commonly during numerous metallurgical operations. In many cases, the operators are unaware of these deadly gases and it is possible that poisoning or death might have occurred without being attributed to them. Phosphine and arsine are characterized by their garlic-like smell. On three occasions, one of the present authors identified them during plant visits in Montana and Quebec and was surprised that the operators did not have any knowledge of these gases.

Recently, in less than two months, a local newspaper in Quebec City reported two serious accidents due to arsine. The first took place aboard a cargo ship while on its way from the USA to Rotterdam; four crew men were poisoned (anonymous, 1974). The second accident took place at a plant in Montreal; five workers were poisoned (anonymous, 1975). Little is published about this problem and most of the information available is found in non-accessible journals. The present review is an attempt to bring this problem to the attention of metallurgists in industry and in government so that proper measures can be taken to avoid unnecessary poisoning or death. Clinical, medical and legal aspects of PH₃ and AsH₃ poisoning are excluded from the review*. Poisoning due to other forms of arsenic, e.g., As₂O₃ dust, arsenate or arsenite ions in water, etc., is also beyond the scope of this review.

Phosphine and arsine ignite in air, even at room temperature, to form oxides and water vapour:

\[ 2\text{PH}_3 + 3\text{O}_2 \rightarrow \text{P}_2\text{O}_3 + 3\text{H}_2\text{O} \]

\[ 2\text{AsH}_3 + 2\text{O}_2 \rightarrow \text{As}_2\text{O}_3 + 3\text{H}_2\text{O} \]

Therefore, they represent a fire hazard. In many cases, the formation of PH₃ and AsH₃ is accompanied by the formation of H₃ and, as a result, the gas mixture represents an explosive hazard when it comes in contact with air. The explosive limits of the mixture are influenced by the PH₃ and AsH₃ content as well as by the H₂ content.

*Numerous reports were found in the literature describing the symptoms, diagnosis, mechanism and treatment of this type of poisoning as well as the legal aspects; these are not discussed here.

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**Table 1** — Threshold-Limit Value of Arsine and Phosphine in Air as Compared to Other Toxic Gases (Steere, 1967)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Formula</th>
<th>Threshold-Limit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>mg/m³</td>
</tr>
<tr>
<td>Arsine</td>
<td>AsH₃</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Phosphine</td>
<td>PH₃</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>HCN</td>
<td>10</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>H₂S</td>
<td>10</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>CS₂</td>
<td>20</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
</tr>
</tbody>
</table>

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Emission of PH₃ and ASH₃ During Metal Recovery and Refined

Phosphorus and arsenic occur in most ores in small amounts. During the processing of these ores, e.g., for metal production, the greater part of these elements may be eliminated in the gasses or the slag, but a trace amount still remains in the metal or its solution as an impurity. It is these traces that are responsible for the formation of PH₃ and ASH₃ when the metal or its solutions are used or processed further. Cases were also reported where arsenic contamination was traced to acids used in metallurgical processes. In general, the emission of PH₃ and ASH₃ in metallurgical processes can take place by the following reactions:

1. Dissolution of a metal containing P or As (as phosphide or arsenide) in acid:
   
   \[ \text{M}_2\text{P}_3 + 6\text{H}^+ \rightarrow 3\text{M}^{2+} + 2\text{PH}_3 \]
   \[ \text{M}_2\text{As}_3 + 6\text{H}^+ \rightarrow 3\text{M}^{2+} + 2\text{ASH}_3 \]
   
   Where M is a divalent metal. Usually the metal also dissolves in acid, generating hydrogen:
   
   \[ \text{M} + 2\text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2 \]

2. Dissolution of a metal in an acid containing traces of As in solution, although the metal itself is arsenic-free. Arsenic may have contaminated the acid during the manufacturing process; e.g., H₂SO₄ produced from pyrite containing traces of As will also contain As. The reaction may be represented as follows:
   
   \[ \text{M}_4\text{P}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{M(OH)}_2 + 2\text{PH}_3 \]
   \[ \text{M}_4\text{As}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{M(OH)}_2 + 2\text{ASH}_3 \]

3. Reaction of a ferrously or an intermetallic compound containing P or As with moisture in the air or water. These reactions may be represented as follows:
   
   \[ \text{M}_4\text{P}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{M(OH)}_2 + 2\text{PH}_3 \]
   \[ \text{M}_4\text{As}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{M(OH)}_2 + 2\text{ASH}_3 \]

4. Decomposition of carbides containing traces of P with water, e.g., Ca₅P₃, which is used for the manufacture of acetylene or in the carburizing of iron.

5. Electrolysis of a solution containing traces of As. In this case, nascent H₂ generated at the cathode reduces arsenious ion in solution to arsine:
   
   \[ \text{AsO}_3^{2-} + 3\text{H}_2 \rightarrow \text{AsH}_3 + 3\text{OH}^- \]

   An accidental case of AsH₃ poisoning that resulted in death was reported by Leelareq and Spriet (1955), which demonstrates the seriousness of the problem. Death occurred 8 days after the victim had cleaned out the sludge from a small tank used for the purification of SO₂, generated by the burning of pyrite, the work having required only 10 minutes. The sludge consisted of 13% FeSO₄, 84% PbSO₄, and 2.6% As₂O₃. Instead of using wooden tools as usual, the victim had used an iron scraper, which showed distinct signs of attack by acid. It was concluded that, in spite of the preliminary washing with water, sufficient acid remained in the sludge to react with the scraper, resulting in evolution of H₂, which reacted with As₂O₃ to form AsH₃. Freitag (1940) and Steel and Feltham (1950) also warned against similar accidents.

HYDROMETALLURGY

Guelman (1925) reported that H₂SO₄ containing as little as 0.045% As₂O₃, and HCl containing as little as 0.0014% As₂O₃, when in contact with Fe, Zn or Sn, may generate dangerous quantities of AsH₃. Muehlicher et al. (1928) showed that AsH₃ was generated by the action of 5% H₂SO₄ on steel, the As being derived from impurities in both the acid and the steel, especially in acid made from sulphide ores. A sample

of 25 l of air taken at the surface of the acid in a pickling tank contained 0.006 mg AsH₃.

In cementation plants, where copper is precipitated from leach solution by scrap iron according to the equation:

\[ \text{Cu}^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{3+} \]

a secondary reaction, namely the dissolution of a part of the iron in the acid, takes place:

\[ \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2 \]

Both reactions result in the formation of PH₃ and ASH₃, and their smell can be readily detected in the neighborhood of these plants, which are usually installed in the open air. A report by Jacobi (1955) mentions this hazard, and one of the present authors detected the smell in one of the plants visited.

A similar situation has also been observed in regard to zinc leach solutions. When metallic Zn containing traces of As is added to cement Cd by the reaction:

\[ \text{Zn} + \text{Cd}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cd} \]

arsine is usually detected. Kohlmayer and Pontani (1935) stressed the danger of AsH₃ emission during that reaction. Firket (1936) reported poisoning and death due to this cause. Firket et al. (1935, 1936) reported further that increasing the acidity or raising the temperature favored the evolution of AsH₃ in the cementation of Cd. Spangenberg and Kotzing (1935) reported AsH₃ formation and cases of poisoning during the purification of ZnSO₄ solution. Further details were given by Batta et al. (1936).

Humperdinck (1939) reported poisoning due to AsH₃ during the leaching of ZnO, although no As was found in the ore. However, the H₂SO₄ used for leaching contained 594 mg/l As and, during leaching, some H₂S was evolved. Gemke and Byxova (1972) also reported the exposure of workers to AsH₃ in a hydro-metallurgical zinc plant.

Bulmer et al. (1940) reported chronic AsH₃ poisoning among workers employed in gold mills using the cyanide process. In this operation, Au is precipitated by Zn dust. Arsine was evolved during the cleaning, with 5% HCl, of the filters used to separate the metal.

A process proposed by Gravenor et al. (1964) for the treatment of low-grade iron ore involves the reduction of the ore to FeO and then leaching with HCl. During leaching, the gas evolved was mainly H₂S, which was accompanied by 0.1% AsH₃.

PYROMETALLURGY

Phosphine and arsine are emitted in pyrometallurgical processing mainly during the refining stage; they are not produced during the process itself, but during the handling and storage of intermetallic secondary products such as drosses and speiss (Koch, 1931). However, Kelleher et al. (1973) mentioned the presence of AsH₃ in blast-furnace gas and proposed a method for its removal by molecular sieves.

Manceau (1929) reported poisoning and death due to AsH₃ when a hot tin dross containing As produced during the pyrometallurgical refining of tin from cassiterite was sprinkled with water and the deadly gas was liberated. Similar reports were later published by Kremer (1931), and Nuck and Jaffe (1932). Poisoning and death by AsH₃ was also reported when Al dross was sprayed with water (Nau et al., 1944, and Dernahl et al., 1944).
In the refining of lead, Al is added to remove As and Sb as a dross. It was found that this dross emits large amounts of AsH<sub>3</sub> as a result of the hydrolysis of aluminum arsenide, when wetted or exposed to moisture. As much as 500 ppm AsH<sub>3</sub> was measured near the dross (Morse and Setterlind, 1950). Cases of death from this operation have been reported by Spoljar and Harger (1950). A related study recently published by Fray (1974) confirmed that AIAs is decomposed with water completely at room temperature, liberating AsH<sub>3</sub>.

Cole and Bennett (1950) reported the presence of about 3 ppm PH<sub>3</sub> in the air in the immediate vicinity of Mg powder after its manufacture from bulk metal which contained 0.0038-0.0093% P. Kipling and Fothergill (1963) reported on AsH<sub>3</sub> formation and cases of poisoning in the aluminum industry. During the recovery of Al from fluorospar slag, AsH<sub>3</sub> was released into the surrounding atmosphere at a level of 5 ppm; the slag contained 10-15 ppm As.

**ELECTROMETALLURGY**

Pyne (1914) discussed the formation of AsH<sub>3</sub> during the electrolysis of CuSO<sub>4</sub> solution containing a small amount of As. This may take place during the electrolysis of Cu from leach solutions or the recovery of Cu from spent electrolyte generated during the electrolytic refining of anode copper. The formation of AsH<sub>3</sub> during the electrodereposition of Zn from ZnSO<sub>4</sub> solution was studied by Pakhomenova and Ovechkinova (1965). It was found that the amount of AsH<sub>3</sub> increases with increasing current density, acidity of electrolyte and As content in solution.

The role of the nature of the surface of the cathode on AsH<sub>3</sub> formation by reduction of H<sub>2</sub>AsO<sub>4</sub> was brought to light by Ramberg (1918). He concluded that the reduction of H<sub>2</sub>AsO<sub>4</sub> takes place more rapidly at spongy than at polished surfaces. Rapid and complete reduction occurs at Hg cathodes.

**Ferroalloys**

A major source of PH<sub>3</sub> and AsH<sub>3</sub> formation is the manufacture and handling of ferroalloys. This has been reported repeatedly for ferrosilicon and ferromanganese and was recently observed by the present authors in the production of ferromanganese. The noxious gases are formed when the ferroalloys, containing traces of P or As as phosphides or arsenides, are contacted with moisture. The reactions proceed very slowly, and thus the gases are produced over an extended period of time. Although their amount may be very small, they may be deadly because of their highly poisonous nature. Repeated cases of poisoning and death, especially aboard vessels carrying ferrosilicon, as well as explosions and fires have prompted some researchers to investigate the cause.

Hamilton (1919) attributed cases of poisoning by AsH<sub>3</sub> to the action of water on ferrosilicon containing 40 to 60% Si. Arsine was reported to be liberated from CaAs<sub>3</sub>, which is present in the ferrosilicon as an impurity. Kurnakov and Urasov (1922) found that not all grades of ferrosilicon were subject to disintegration and the emission of the poisonous gases during storage, but only those containing 33.3 to 75% Si, and especially alloys with 50 to 60% Si. However, ferrosilicon has a strong tendency to segregate during casting and, as a result, the difference in silicon content between the top and the bottom of the ingot may vary greatly. It was also established that pure Fe-Si alloys do not disintegrate in air, regardless of their Si content. Also the presence of up to 0.04% P in the alloy does not lead to the formation of PH<sub>3</sub>. It was the simultaneous presence of 0.03-0.04% P and 3% Al in the alloy that caused disintegration and emission of PH<sub>3</sub>, although a Fe-Si alloy containing 5% Al was quite stable.

Schut and Jansen (1982) also reported deaths on board a freighter carrying ferrosilicon and reported that not only was PH<sub>3</sub> emitted from this ferroalloy, but also AsH<sub>3</sub>. They determined the amounts of these gases emitted from different samples of ferrosilicon and concluded that alloys containing 40 to 60% Si were the most dangerous.

Delomenie (1933) found also that the formation of PH<sub>3</sub> and AsH<sub>3</sub> depended on the composition of ferrosilicon, as shown in Table 2. He attributed the formation of these gases to the presence of Ca and Al in the alloys, because a pure alloy of 50% Si remained compact and unaltered in moist air and the addition of these impurities caused disintegration.

**TABLE 2 — Formation of Poisonous Gases from Ferrosilicon When in Contact with Water (Delomenie, 1933)**

<table>
<thead>
<tr>
<th>Silicon Content in FeSi Alloy, %</th>
<th>Gases Formed, liter/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>20 - 30</td>
<td>2000</td>
</tr>
<tr>
<td>30 - 60</td>
<td>little</td>
</tr>
<tr>
<td>&gt; 60</td>
<td>much</td>
</tr>
</tbody>
</table>

Barnabishvili (1938) discussed the emission of PH<sub>3</sub> from FeMn and Jöttén (1942) discussed the emission of PH<sub>3</sub> and AsH<sub>3</sub> from FeSi and FeSiMn by the action of moisture, mentioning the precautions taken to avoid poisoning.

Trota and Maksimenko (1948), on the other hand, found that Fe-Si alloys containing 71.7 to 77.5% Si also emitted appreciable amounts of PH<sub>3</sub>. The alloys studied by these workers contained 0.020 to 0.027% P and were ground to ~150 mesh, then boiled in distilled water for 10 hours. When the gases evolved were collected and analyzed, they were found to contain 0.1-0.3% PH<sub>3</sub> with the balance being H<sub>2</sub>. The volume of gases evolved varied between 16 and 27 l/kg of alloy. Between 13 and 34% of the phosphorus present in the alloy was evolved as PH<sub>3</sub>. They also observed that some PH<sub>3</sub> was formed during dry grinding in a tightly closed mill. After 4 hours of grinding, the gas contained 0.56% PH<sub>3</sub>, 1.75% H<sub>2</sub>, 16.55% O<sub>2</sub> and 81.14% N<sub>2</sub>. These authors also pointed out the explosion hazard of a H<sub>2</sub>-O<sub>2</sub> mixture due to the presence of PH<sub>3</sub>. A mixture is explosive when it contains 9-64% H<sub>2</sub>; in the presence of 7% PH<sub>3</sub> the explosive limit is 6-75%.

Presruder (1951) noted the escape of PH<sub>3</sub> from a crack in the center of a 50% ferrosilicon cast. Disintegration occurred when the Si/Fe ratio was greater than 1.04; it proceeded immediately when the Al content of the alloy exceeded 1.7% and was delayed when it was below 0.75%. It is believed that Al plays an important role in decomposition and that aluminum phosphide is decomposed by moisture, liberating PH<sub>3</sub>.

Zotkin and Kramarov (1957) also reported that certain alloys of ferrosilicon stored outdoors disintegrated into a powder, with evolution of PH<sub>3</sub>. They

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showed that ferrosilicon containing 55-65% Si had the highest tendency to decompose. If the phosphorus content is below 0.03%, however, no decomposition occurred at any Si content. Decomposition in water is more intensive than in air. To prevent the formation of PH₃, they recommended that ferrosilicon should be stored under vacuum, or under a layer of paraffin, immediately after casting.

Dalgaard and Gregersen (1963) gave further details on PH₃ and AsH₃ formation from ferrosilicon under damp conditions and reported deaths from this source. Arkhangel'skaya (1963) warned against Fe-Si dust. Wefers (1963) mentioned that the presence of impurities in the ferrosilicon facilitated the formation of arsine.

**Other Sources**

Hazards due to PH₃ during the use of acetylene in welding have been known for a long time. Eichler (1934) attributed the poisoning of a worker in a welding shop to PH₃. Technical acetylene produced by the reduction of CaC₂ with water contains traces of PH₃, and leaks of this gas can be deadly for that reason. The PH₃ can be traced back to the traces of phosphorus present in the raw material charged to the electric furnace used to manufacture the carbide. This hazard was also recently mentioned by Hoschek (1966). The phosphine content of acetylene has an effect on the welds. Holzhauser (1930) showed micrographs illustrating the structure of such welds. In some metallurgical plants, CaC₂ is used as a desulphurizing agent for iron. This practice is highly hazardous, because of the emission of PH₃ during the handling and storage of CaC₂.

Phosphine has been detected during the machining of spheroidal graphite iron (Mathew, 1961; Adam, 1967). It has also been mentioned to be present in the atmosphere of wire-drawing factories for making metal screens (Gorbunova and Shaposhnikova, 1970). Kohlmeyer and Pontani (1935) reviewed the possibilities of the production of AsH₃ during metal refining processes and mentioned galvanizing — i.e., the covering of iron with a thin layer of zinc for protection against corrosion — in particular.

Proshkina (1971) reported on the formation of PH₃ at the level of 0.6-0.8 mg/m³ during the crushing and flotation of phosphorite ores. Zhakashov (1973) mentioned that PH₃ concentrations in the neighbourhood of a phosphorus plant were much higher than the maximum permissible concentrations. Amelin and Patrushev (1970) reported that the waste gases of electric furnaces for the reduction of phosphorite to manufacture elemental phosphorus always contain PH₃. This was attributed to the presence of moisture and water of crystallization in the raw material as well as hydrocarbons from coke. The formation of PH₃ was attributed to the reaction:

\[ 2P + 3H₂ + O₂ \rightarrow 2PH₃ + 3CO \]

By replacing coke by graphite and by using dried charges, the formation of PH₃ was eliminated, thus avoiding air pollution and at the same time increasing the phosphorus production. Ershov et al. (1974) reported that phosphine is formed on the elektrotaktic precipitators in the industrial preparation of elemental phosphorus and that the gases contain 0.03 to 0.05% PH₃.

An uncommon appearance of PH₃ was reported by Steffens (1925) when mortar in an old building emitted the poisonous gas on treatment with water. The formation was ascribed to the action of water on Ca₃P₂, probably formed from the Ca₃(PO₄)₂ which was originally present. It is possible, however, that microorganisms played a role in the formation of PH₃. Arsenic compounds related to arsine, e.g., ethyl arsine, AsH₃(CH₃), are formed by the action of microorganisms on other arsenic compounds. Husse (1913), for example, mentions *Penicillium brevicanum* and others, and Zussman et al. (1961) mention *Trichophyton rubrum*.

**Conclusion**

The emission of phosphine and arsine in the metallurgical industry is a common phenomenon and, under special circumstances, may constitute a serious health, fire and explosion hazard. The seriousness of the problem is further aggravated by the lack of knowledge about the formation of these gases among operators and management in the metallurgical industry.

Operators in metallurgical plants should determine, on a routine basis, the P and As contents in all raw materials, such as acids, ores, scrap, etc., and trace their behaviour through all processing stages to the finished products. Secondary products, such as dust, spessis and ferroalloys, should be analyzed and handled appropriately. Special attention should also be devoted to electrolytic processes from aqueous solution whereby H₂ is evolved, because AsH₃ is liable to contaminate the gas. Analytical techniques should be developed to cope with the situation.

The authors believe that the use of Ca₃P₂ as a desulphurizing agent for molten iron should be discontinued, due to the formation of PH₃ during its storage and handling; no doubt a substitute could be found. The possibility of leaks from acetylene tanks and the use of acetylene in general, e.g., in welding, pose hazards about which operators should be well informed.

Whenever a possibility exists that gives rise to the emission of these gases, precautionary measures should be taken, e.g., proper ventilation, first-aid facilities and periodic medical examinations, etc., and government authorities should ensure that industry is fulfilling its obligations in this respect according to guidelines designed to protect the workers. Also, the transportation of material liable to emit these gases by contact with moisture, in particular dross, spessis and ferroalloys, should be strictly regulated to protect the public.

**Acknowledgment**

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**Bibliography**


*Acetylene itself is nontoxic, but it is a "simple asphyxiant"; i.e., when present in high concentrations in air, it acts primarily as an asphyxiant without other significant physiologic effect. A threshold-limit value may not be recommended for a simple asphyxiant, because the limiting value is the available oxygen.*