Pollution Problems in the Metallurgical Industry

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Pollution problems in the metallurgical industry are numerous and serious but they can be readily solved. In fact some of these problems have been already solved and adopted on commercial scale but not widely used. It is hoped that this review will enhance the diffusion of knowledge in this field so that the standing problems may be eventually solved.

Emissionsprobleme in der Metallindustrie sind zahlreich und bedenklich, aber sie sind lösbar. Tatsächlich wurden verschiedene Probleme bereits gelöst und ins Verkaufsprogramm aufgenommen, aber bisher nicht genügend angewandt. Dieser Artikel soll dazu beitragen, das Wissen auf diesem Gebiet zu verbessern, um die anstehenden Probleme lösen zu können.

Introduction

Earlier metallurgical industry used to emit waste gases directly at ground level, e.g., roasting of sulfide ores or making of coke by the beehive method. Later on, stacks were built high enough only to provide adequate draft for furnaces. Operations were usually established in isolated areas. As the scale of operations increased, and as lands
near industry were inhabited and cultivated by farmers, smoke stacks created problems. Poisonous or irritant gases as well as particulates emitted by these stacks, posed serious danger to the vegetation and animal life in their vicinity. Court-ordered shut downs and compensation to farmers became common. Thus, at one time, smoking chimneys were a welcome sign of prosperity and meant prestige to a country, it is now considered a disaster area by many. Beside government legislation against pollution, residents in many communities now protest against the erection of industrial plants in their regions.

Stack emission may represent a considerable cost to the plant itself because of the loss of particulates which are sometimes valuable, and also because of exposing the equipment to a corroding atmosphere. The major pollution problems arise in iron and steelmaking, in the treatment of nonferrous sulfide ores, and in the aluminum industry. There are also some industries in which deadly gases such as phosphine and arsine are emitted within the plant itself and may affect the health and comfort of the workers. In many cases, operators and management lack knowledge about their formation. Also, some operations handling ores containing radioactive elements are polluting the environment.

As rich ores became exhausted, the industry was forced to use low grade ore. Flotation is an efficient method for concentrating these ores. Waste material from this operation, i.e., tailings in form of slurry is channeled into ponds to settle the solids and the water is recovered. As the solids accumulate, a tailing dump covering many acres is formed. Surface drying of the dump and high winds may result in localized dust storms. An effective way of preventing these storms is by keeping the dumps wet at all times. Nowadays, planting and cultivation of shrubs and trees to act as windbreaks are more appealing.

A problem in the metallurgical industry that is shared by many other industries is the oxides of nitrogen NO and NO₂ (usually expressed as NO₃). These gases are always formed when atmospheric air is heated to a high temperature in a fuel combustion process; the higher the temperature the higher is the yield of NO₃. Although the concentration of NO₃ in the stack gases is in the order of 10 - 200 ppm, the actual amount is high because of the large volumes of gases discharged.

Iron and Steelmaking

Pollution in the iron and steel industry is severe because of the large tonnage of material treated. The major sources of pollution are the following:

Manufacture of coke

Coke is an essential raw material for the manufacture of iron in the blast furnace; about 0.6 ton is needed for making 1 ton pig iron. It is made by heating coal in air-tight ovens to get rid of its volatile constituents and to obtain a hard and porous carbonaceous material suitable for withstanding the weight of the charge in the furnace without being crushed to powder. Pollution during the manufacture of coke stems from the following sources:

1. Emission of dust and poisonous gases, e.g., CO, H₂S, hydrocarbons, etc., during charging and discharging the furnaces, i.e., when the lids are opened to dump the coal in, and when the doors are opened to push away the coke.

2. Emission of dust and poisonous gases during the quenching of the red hot coke with water to cool it and to prevent its combustion.

3. Non-condensable gases leaving the oven contain H₂S and other organic sulfur compounds which originate from the sulfur in the coal. These gases are usually burned to supply heat for the same ovens, or for boilers and other installation. Waste gases from these operations will therefore contain SO₂. Only few plants remove H₂S and the organic sulfur compounds before utilizing these gases as a fuel.

There have been some attempts to reduce the pollution from these sources. For example, improving the coal charging system, or quenching the hot coke by an inert gas in a closed system, but these modifications have not yet been widely adopted.

Steelmaking

1. During the manufacture of steel by the open hearth process, fluor spar, CaF₂, is used as a flux; its consumption is about 1.8 Kg/t steel. The presence of water in the combustion gases in the furnace results in the decomposition of about half the CaF₂ to form the volatile HF gas according to:

\[ \text{CaF}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HF} + \text{CaO} \]

which finds its way in the stack. Hydrogen fluoride concentration in the stack gas is about 3000 ppm which is thousand times higher than the accepted threshold limit value for human exposure. About 100,000 tons of hydrogen fluoride are emitted annually from this source. Fluorosis in cattle or damage to vegetation has occurred in the vicinity of iron and steel plants. Removal of HF from the stack gas is essential. Other steel-making processes are now competing with the open hearth process, because of this problem, or a flux other than fluor spar has to be found.

2. During the manufacture of steel by oxygen top blowing (LD Process) thick brown fumes of iron oxide are formed. Because of their extremely fine particle size they are difficult to remove from the stack gases and thus cause nuisance to the inhabitants of the neighborhood. Bottom oxygen blowing process is now competing with the LD Process because of this, among other reasons.

Ferroalloys

Ferroalloys are used as additives to steel. They are manufactured by the simultaneous reduction of iron ore and another oxide ore mixture. Thus, for example ferromanganese is produced by the reduction of FeO and MnO mixtures. Ferrosilicon is produced by the reduction of FeO and SiO₂ mixture, etc.

Ferroalloys usually contain small amounts of phosphorus and arsenic as impurities which are traced back to the raw materials from which the alloys are manufactured. During crushing and storage, both P₂O₅ and As₂O₅ are liberated due to reaction with moisture in the air. The reactions taking place may be represented as follows:

\[ \text{Fe}_{2} \text{P}_{2} + 6 \text{H}_2\text{O} \rightarrow 3 \text{Fe(OH)}_3 + 2 \text{PH}_3 \]

\[ \text{Fe}_{2} \text{As}_{2} + 6 \text{H}_2\text{O} \rightarrow 3 \text{Fe(OH)}_3 + 2 \text{AsH}_3 \]

These reactions proceed slowly thus the noxious gases are produced over an extended period of time. Although their amount may be very small, yet they may be deadly because of their highly poisonous nature. Phosphine and arsine are characterized by a garlic-like smell; they ignite in air and therefore represent a fire hazard. In many cases, their formation is accompanied
by the formation of hydrogen and as a result the gas mixture represents an explosive hazard when it comes in contact with air. Numerous cases of poisoning and death especially aboard vessels carrying ferroalloys, as well as explosions and fires were reported from this source.

**Treatment of Sulfide Ores**

During the recovery of copper, lead, and zinc from their sulfide ores, SO₂ is formed in large quantities. The problem associated with this gas is twofold:

1. About 30 % of this gas is actually utilized to make H₂SO₄ and the rest is emitted in the atmosphere. Sulfur dioxide is emitted because its concentration in the exit gases is only 1 - 2 % which is too low to be utilized directly for making acid. About 14.6 million tons of SO₂ from this source were emitted in the environment in 1970. It is estimated that double this amount will be emitted in 1980 if no corrective measures are taken.

2. Sulfide ores normally contain small amounts of mercury, arsenic, selenium, and tellurium. These impurities either go to the process gases used to make H₂SO₄, or are emitted in the atmosphere. In both cases, there is the possibility of their entering in the nutrition cycle. Hence, processes have to be developed to cope with this hazard since these metals are highly poisonous.

The first problem is not new. In the 1940's extensive research was done, pilot plants were built, and commercial scale plants went into operation to utilize SO₂ instead of emitting it in the environment. Most of these operations, however, were later discontinued for a variety of reasons. In the early 1960's there was a shortage in the supply of elemental sulfur while the need for H₂SO₄ production was growing, and thus the problem was revived. Recently, however, the situation of elemental sulfur has changed due to the development of natural gas production in Alberta, Canada. Large amounts of H₂S contaminating the gas has to be separated and converted to elemental sulfur before the gas is suitable for consumption. About 2 million tons of sulfur from this source is produced every year. As a result the supply exceeds the demand and new uses for the element are sought.

**Recovery or disposal of SO₂**

There have been numerous attempts to solve these problems and much research is being done for this purpose. However, processes aimed at solving the problem of SO₂ in smelter gases by obtaining highly concentrated SO₂ suitable for liquefaction, or exit gases rich in SO₂ that are suitable for H₂SO₄ manufacture, must assume the existence of a nearby market for either the liquid SO₂ or the acid. Because of the seriousness of the problem, it has been even considered to change existing technology and to seek new processes in which SO₂ is not a reaction product. Processes yielding elemental sulfur would be ideal because sulfur is easy to store, cheap to transport, and can be converted to SO₂ or H₂SO₄ readily when needed arises. In this respect hydrometallurgy offers a promising approach. Processes yielding H₂S would also be interesting since H₂S can be converted readily to elemental sulfur according to:

\[ \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} \]

Attempts to solve the SO₂ problem have been so far along the following lines:

1. **Improving existing technology.**
   a) Improving sulfuric acid production technology such that smelter gases containing only 1 % SO₂ can be used instead of those normally used (~ 10 % SO₂).
   b) Improving existing pyrometallurgical processes such that SO₂ emitted is minimum, e.g., collecting efficiently the gas emitted during converting white metal, or utilizing electric furnaces instead of reverberatory furnaces.

2. **Modifying existing technology** such that SO₂ concentration in the exit gases is high and economical to recover, e.g., oxidation of the sulfides by pure oxygen, or oxygen-enriched air.

3. **Disposal of SO₂ without polluting the environment.** This can be achieved by absorption by a solid, e.g., CaO or CaCO₃ to form CaSO₃:

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{CaO} \rightarrow \text{CaSO}_3 \]

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{CaCO}_3 \rightarrow \text{CaSO}_3 + \text{CO}_2 \]

The difficulty with this suggestion is the requirement and handling of large tonnage of solid; about three tons of lime and stone and over four tons of waste CaSO₃ have to be discarded for the elimination of one ton of sulfur.

4. **Utilization of SO₂**
   a) By converting into dilute H₂SO₄ using catalytic oxidation in aqueous phase.

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]

Mn²⁺ or Fe²⁺ are used as catalysts. Acid produced is 10 - 15 % H₂SO₄ which can be eventually concentrated to 70 % by a series of recycling and submerged combustion.

b) By absorption in ammonium hydroxide to form ammonium sulfate which can be marketed as fertilizer:

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 + 2 \text{NH}_3\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O} \]

A variation of this technique is converting SO₂ catalytically to SO₃ then injecting NH₃ vapor in the gas stream to form fine crystals of ammonium sulfate that can be separated in bag filters.

c) By absorption in a raw material to transform it into a useful product, e.g., absorption in phosphate rock to yield superphosphate fertilizer.

d) By absorption selectively by a liquid or a solid that it capable of desorbing it in a concentrated form under other set of conditions, so that the SO₂ so obtained can be liquified or used for H₂SO₄ manufacture. Water is a cheap absorbent; solubility of SO₂ is 228 g/l at 0°C and 5.8 g/l at 90°C. About one ton water is required for the absorption of 1 ton SO₂. A more efficient absorbent is dimethyl aniline (p. 194°C) and it has been used industrially. Tributyl phospate has also been suggested. Solids suggested include activated charcoal (adsorbs ~380 cc/g at 15°C), and synthetic zeolites (sodium aluminum silicates). When charcoal is used, regeneration is achieved by washing with water to form dilute H₂SO₄. In case of zeolites, heating at 360°C - 375°C supposedly expels the SO₂.

Further, absorption of SO₂ from smelter gases by many reagents results in the formation of sulfites which can be decomposed to regenerate the reagent and yield concentrated SO₂. However, SO₂ is always accompanied by a large excess of O₂ such that sulfates and sulfites will be formed. Sulfates are difficult to decompose since high temperature is needed, and therefore regeneration will not be complete.

e) By interaction with a solid or a liquid which is then treated in numerous steps to yield H₂S which can be converted readily to elemental sulfur. Suggested reagents are: solid sodium aluminate, aqueous solution of sodium citrate, molten mixture of Na₂CO₃ - Li₂SO₄ - K₂CO₃ (one third of each, m. p. 397°C). In these systems, smelter gases containing small amounts of SO₂ and large excess of O₂ combine to form alkali sulfate which is then reacted by H₂ to generate the reagent and simultaneously form H₂S.

f) By reduction with carbon or natural gas to elemental sulfur. This is an ideal way to dispose of SO₂; however, a preconcentration step of SO₂ is essential. Reduction takes place at 1200°C according to:

\[ \text{SO}_2 + \text{C} \rightarrow \text{S} + \text{CO}_2 \]

\[ 2 \text{SO}_2 + \text{CH}_4 \rightarrow 2 \text{S} + \text{CO}_2 + 2 \text{H}_2\text{O} \]
Elimination of metallic impurities from smelter gases

An appreciable amount of As, Se, and Te is volatilized during the treatment of sulfide ores and most of these are collected in the dust recovery system. But mercury which is also volatilized and is present in the exit gases is not removed by such system because of its much lower concentration. To condense mercury, the gases have to be cooled to at least -10°C which is economically out of question. Processes have been developed to cope with this problem but they are not yet widely adopted. The following can be mentioned:

1. The Outokumpu Process
   This process was developed by the Outokumpu Company in Finland and has been in commercial operation since 1970 at the company’s zinc smelter at Kokkola. Sulfur dioxide gas obtained by the oxidation of zinc sulfide concentrate and containing 40 to 80 ppm Hg is cooled in waste heat boilers, then its dust content is removed in cyclones and electrostatic precipitators. The gas at 350°C is then cooled in heat exchangers to about 200°C using concentrated H₂SO₄ as a heat exchange medium. It is then scrubbed with the same acid which is now at 150 to 200°C to convert elemental mercury into a sulfate. The acid is recycled and becomes saturated in HgSO₄. As a result, crystals of HgSO₄ precipitate and can be separated in thickeners.

2. The Bolden Processes
   The Bolden Kemi Company in Sweden has developed numerous processes for the removal of mercury from SO₂ obtained by the roasting of pyrite. In one of these, red amorphous selenium is deposited from an aqueous solution of seleniumic acid on a porous ceramic material which is then used as a filter for the gas. Mercury in the gas is deposited in the filter as HgSe. In another, a slurry of amorphous selenium is used to scrub the gases and precipitate HgSe. Active carbon filters are also used to adsorb mercury vapor from the gas. Mercury was also precipitated from sulfuric acid of certain concentration (= 85% H₂SO₄) by injecting sodium thiosulfate solution. Under these conditions, elemental sulfur is formed which reacts with mercury forming HgS which can then be filtered.

3. Det Norske Zinkkompani in Norway has collaborated with Bolden Kemi. It is based on the scrubbing of the gases by a solution of mercuric chloride. Any mercury in the gas will react forming mercurous chloride which is precipitated and filtered.

4. Cenim Process
   This process was developed at the Centro Nacional de Investigaciones Metalurgicas in Madrid to recover the traces of mercury in the stack gases at Almadén mercury plant. Mercury ore from the Almadén mine is heated in the usual way in rotary kilns to volatilize mercury vapors. After cooling the gases and condensing the mercury, the gases leaving the condenser contain about 70 ppm Hg. The recover this mercury and to prevent pollution of the neighborhood of the mine, the stack gases are washed with a solution of sodium thiocyanate whereby two thirds of the mercury is dissolved as the thiocyanate complex and one third precipitates as HgS. To achieve a complete precipitation of mercury in the form of HgS and at the same time to regenerate the sodium thiocyanate solution, a stoichiometric amount of sodium sulfide solution is added to the solution.

5. St. Joe Process
   This process has been developed by St. Joe Minerals Corporation, USA and has been in commercial operation at the company’s zinc smelter at Monaca, Pennsylvania since 1973. In this process mercury vapor emitted during roasting of zinc sulfide concentrate is precipitated from the gas phase as mercury sulfide powder which is then separated as a slurry in washing tower. The precipitation of HgS is achieved by injecting a controlled amount of hydrogen sulfide in the gas stream.

6. Toho Process
   This process has been developed by the Toho Zinc Company in Japan and has been in commercial operation since 1973 at Toho’s Chigirishima lead smelter and Onahama zinc smelter, both in Japan. It is also used at St. Joe’s zinc smelter in Monaca, Pennsylvania as a second stage operation to remove the last traces of mercury in the sulfuric acid produced after removing the bulk of the mercury in the SO₂ gases by the H₂S injection method described above. The Toho Process is based on precipitating mercuriic iodide, HgI₂, by adding potassium iodide.

The Aluminum Industry

Manufacture of sodium hydroxide

Alkali industry is probably the largest single source of mercury pollution; it handles a large tonnage of mercury in the metallic form which is used as cathode in cells electrolysing sodium chloride solution. Sodium hydroxide produced in these cells according to the reaction:

\[ \text{Na}(\text{Hg})_2 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 + x\text{Hg} \]

is used in metallurgical plants treating bauxite to obtain pure Al₂O₃ suitable for the manufacture of aluminum. The problem is mainly a handling problem, e.g., spillage, draining, evaporation, etc. Also, the hydrogen evolved in the above reaction is contaminated by traces of mercury vapor. This mercury should be removed so that it is not introduced to other industries. This is easy to do by scrubbing the gas; there is no easy way, however, for removing the traces of mercury in the caustic produced.

Electrolyzing sodium chloride solution using a diaphragm cell and solid electrodes, e.g., the Hooker cell permits the formation of sodium hydroxide at the cathode and chlorine at the anode. This process avoids the use of mercury and is less energy-consuming than the mercury cell. However, the sodium hydroxide produced is less pure since it is contaminated by sodium chloride and is dilute. The cost of evaporation to increase its concentration is high.

Leaching

A product of the aluminum industry which is at present considered as waste is the red mud. This is the residue produced after leaching the bauxite with sodium hydroxide. It is composed mainly of Fe₂O₃, TiO₂, SiO₂, some hydrated sodium aluminum silicates, and other gangue minerals. The stock piles of red mud represent an environmental problem to the aluminum industry, and methods to utilise this material should be found.

Manufacture of carbon electrodes

Carbon electrodes for electric furnaces are of two types: prebaked or baked-in-place. In the first type the electrodes are manufactured in a special plant and used in the furnace as needed. In the second type, also called Soderberg electrodes after their inventor, the carbon paste is added periodically into a large casing and the heat released from the furnace (cell) bakes the paste into a solid anode. In both cases, the electrode is composed of coke bound with pitch. During the baking process, some of the pitch components volatilize causing pollution of the environment. This problem is specially critical in the aluminum industry due to the large consumption of both types of electrodes.

Reduction

During the production of metallic aluminum, CO and CO₂ are formed as a result of the electrolytic reduction of Al₂O₃ by the carbon electrodes. These gases which are composed of 20 to 40% CO and 80 – 60% CO₂ are generally not considered harmful to the environment because CO is usually burned to CO₂ before leaving the stacks. However, they always contain a small amount of fluorine compounds calculated at about 30 Kg fluorine per ton Al produced. Reminding that the world production of Al is about 8 mil-
Similar reactions take place during the recovery of cadmium from ZnSO₄ solutions by cementation with Zn dust. Also, during the electrolysis of a solution containing traces of As, nascent H₂ generated at the cathode reduces arsenious ion in solution to arsine.

AsO₃³⁻ + 3 H₂ → AsH₃ + 3 OH⁻

Copper, zinc, and cadmium are recovered by the electrolysis of their aqueous solutions, and the formation of AsH₃ was observed and caused death in some cases.

**Hydrometallurgy of Gold**

Gold ores are usually treated by the amalgamation process to recover the large gold particles and this is followed by the cyanidation process to recover the remaining gold. Both processes are highly hazardous because of the toxicity of mercury as well as the cyanide solution. Handling of mercury requires strict management to avoid its spilling and disposal in streams, or emitting its vapor to the atmosphere during the separation of gold from the amalgam by distillation. Akalinity in cyanide leach solutions should be carefully maintained to avoid the liberation of HCN into the surroundings by atmospheric CO₂ according to the equation:

2 CN⁻ + CO₂ + H₂O → 2 HCN + CO₃⁻

It is common practice in cyanide mills to dispose of a part of the cyanide from time to time to prevent the accumulation of impurities which may interfere with the leaching step. This bleed solution should never be thrown into the streams without prior treatment because of its extreme toxicity. Two methods of disposal are usually used:

a) Oxidation of CN⁻ to NO₃⁻ which is harmless,

b) Acidification to liberate HCN which is then absorbed back in alkalai to form alkalai cyanide for recycle.

Some gold ores are associated with the mineral arsenopyrite. These cannot be treated directly by conventional methods because of the excessive consumption of reagents, therefore they are usually roasted to eliminate as much as possible of the arsenic and sulfur which are usually emitted to the atmosphere.

**Treatment of Ores Containing Radioactive Elements**

**Uranium ores**

When sulfuric acid is used as a leaching agent for uranium ores, about 90% of the radium, which is a decay product of uranium, remains in the residue. When radium was in need, the residue was treated for its recovery. The situation, however, has changed since many years, radium is no longer in demand and therefore the residues from uranium plants are at present stockpiled. Radium decays into the radioactive gas radon. The diffusion of this gas in the environment, the scattering of radioactive dust particles by wind, and erosion of the piles of residues by water, represent a serious pollution problem. A typical disposal pond contains 0.6 mg Ra per ton of solids. Abandoned mill sites are particularly hazardous because tailings dams may either erode or rupture and release tailings to streams. Therefore, controlled storage of uranium mill residues must be continued after the life of the mill to safeguard the environment from radioactive pollution. Considering the 1622-year half-life of Ra, storage must be controlled for many thousands of years to enable abatement of the radiation hazard by natural decay of radium and its products. For these reasons, leaching uranium ores with HNO₃ or HCl followed by precipitation and separation of (Ra, Ba)SO₄ by adding BaCl₂ is being considered as a means to solve this problem although these acids are more expensive than the commonly used H₂SO₄.

**Other ores**

Radioactive hazard in the environment is not restricted to the residues from the treatment of uranium ores alone. There are certain ores that are treated for other metals but contain traces of uranium or thorium and during the metal recovery process the radioactive elements are rejected as slag. For example, pyrochlore is a niobium ore that contains small amounts of uranium and thorium; it is used mainly for manufacturing ferrochromium. During the reduction step, a slag is obtained containing most of the uranium and thorium. Such slags are presently stockpiled and represent a pollution hazard.

**Welding**

Calcium carbide, CaC₂, is an important industrial material produced on a large scale by heating lime with coke in an electric furnace. It has two major uses: manufacture of acetylene used in welding, and in the carburization of molten iron. The carbide contains traces of P as an impurity which was present in the raw materials. When it is decomposed by water to manufacture acetylene, PH₃ is formed. Thus technical acetylene contains traces of PH₃ and leaks of this gas can be deadly for that reason¹. Cases of poisoning have been reported in welding shops. Even during storage and handling, the carbide reacts with moisture in the air to form PH₃.

¹) Acetylene itself is nontoxic but it is a "simple asphyxiant", i.e., when present in high concentrations in air, it acts primarily as asphyxiant without other significant physiologic effect. A threshold limit value may not be recommended for a simple asphyxiant because the limiting values is the available oxygen.
Boliden Process - charcoal filters for mercury removal from $\text{SO}_2$ gas.