Clean Technology in the Metallurgical Industry*

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Abstract

In the middle of the 1960s environmental groups started pressing for cleaner environment. The metallurgical industry responded in a variety of ways. The steel industry closed open hearth furnaces and switched over to other cleaner technology. The aluminium industry switched over from Soderberg to pre-baked electrodes in the electrolytic cells. The copper industry abandoned the reverberatory furnace to a flash smelting technology. Tall stacks were constructed to dispose of SO_2, but the zinc industry eliminated SO_2 emissions completely by using pressure leaching technology which may well be applied to other nonferrous industries. Some other measures taken are reviewed.

INTRODUCTION

Beside government legislation against pollution, residents in many communities now protest against the erection of industrial plants in their regions. The construction of tall stacks has been a new development in the past decades. The tallest stack in the world has been constructed in Sudbury, Canada. It is 381 m high – as high as the Empire State Building (Fig. 1). The problem of dust has been generally solved by adding efficient scrubbers and electrostatic precipitators. This not only improved the local environment but also allowed the recovery of valuable particulates. In most cases the value of these particulates offsets the capital investment in the dust recovery system.

The metallurgist is now trying to cope with the environmental problems by adding new equipment in existing plants that would abate pollution, by improving equipment design, and in some cases is forced to develop new processes that are less polluting than the conventional ones. Closely related to these attempts is the need to conserve the national resources through recycling of scrap metal, valorization of mineral waste, and recovery of metals that would otherwise be lost in process streams [1, 2].

Fig. 1. INCO 381 m high chimney in Sudbury, Ontario constructed in 1972 as compared to other chimneys constructed earlier.

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IRON AND STEEL

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 t is needed for making 1 t pig iron. Pollution during the manufacture of coke stems from the following sources:

• Emission of dust and poisonous gases, e. g., CO, H_2S, 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.

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

• Non-condensable gases leaving the oven contain H_2S and other organic sulphur compounds. 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 SO_2. Few plants remove H_2S and the organic sulphur compounds before utilizing these gases as a fuel.

There have been some attempts to reduce pollution from these sources. For example, quenching the hot coke by an inert gas in a closed system (Fig. 2), but this modification has not yet been widely adopted [3].

Manufacture of iron

During the manufacture of iron in the blast furnace, some hydrogen cyanide, HCN, and cyanogen gas, C_2N_2, are formed as a result of the reaction of nitrogen in the blast with coke. Blast furnace gas contains 200–2000 mg/m^3 of these cyano compounds which are highly toxic. In the dust collecting system, the gases are scrubbed with water and some of this water finds its way in waste disposal. Before discharging this water, cyanide compounds dissolved in it must be destroyed. Blast furnace slags contain CaS which originates mainly from the sulphur in the coke. It emits H_2S during quenching and stock piling. H_2S has the smell of foul eggs and is highly poisonous.

Steelmaking

Open hearth process. During the manufacture of steel by the open hearth process, fluorspar, CaF_2 was used as a flux. The presence of water in the combustion gases in the furnace results in its decomposition to form HF gas, which finds its way in the stack. Hydrogen fluoride concentration in the stack gas was about 3000 ppm. About 100 000 t of hydrogen fluoride were emitted annually from this source. Fluorosis in cattle or damage to vegetation has
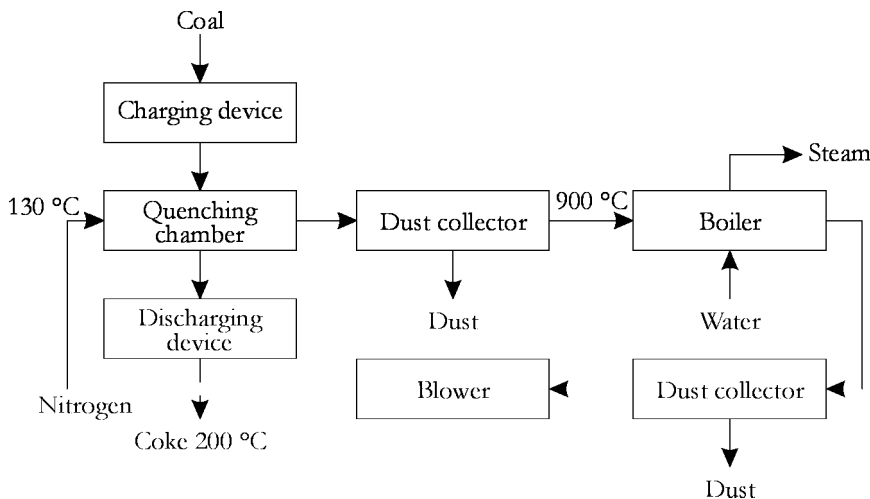
Fig. 2. Quenching coke by nitrogen in a closed circuit and recovering the heat to generate steam.

occurred in the vicinity of iron and steel plants. This was one of the reasons why this process has been abandoned in the 1970s.

Oxygen steelmaking. 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 were difficult to remove from the stack gases and thus they cause nuisance to the inhabitants of the neighbourhood. Bottom oxygen blowing process is now competing with the LD Process because of this, among other reasons.

Pickling. Before surface treatment, steel must be pickled, *i. e.*, treated in an acid solution to remove the thin oxide film. Sulphuric acid was universally used for this purpose because it was the cheapest acid. The waste acid, now containing ferrous sulphate, was thrown away. With increased regulations, the waste acid was neutralized by lime at the same time precipitating the iron before disposal. It became a costly operation. The problem was solved in the 1960s by switching over to hydrochloric acid instead of sulphuric, although it was more expensive. The reason was that ferrous chloride could be economically converted to Fe_2O_3 which is suitable as pigment, and HC1 for recycle by oxyhydrolysis:

$$2FeCl_2 + 2H_2O + 1/2O_2 \rightarrow Fe_2O_3 + HCl$$
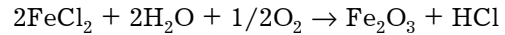
Electric furnace dust. During the production of steel in electric furnaces, traces of zinc in the charge volatilize due to the high temperature and condense in the dust collecting system as fine particles. This dust was usually discarded or used as landfill. However, it was realized later that zinc in the dust may be solubilized and contaminates surface or subterranean water. Processes were therefore
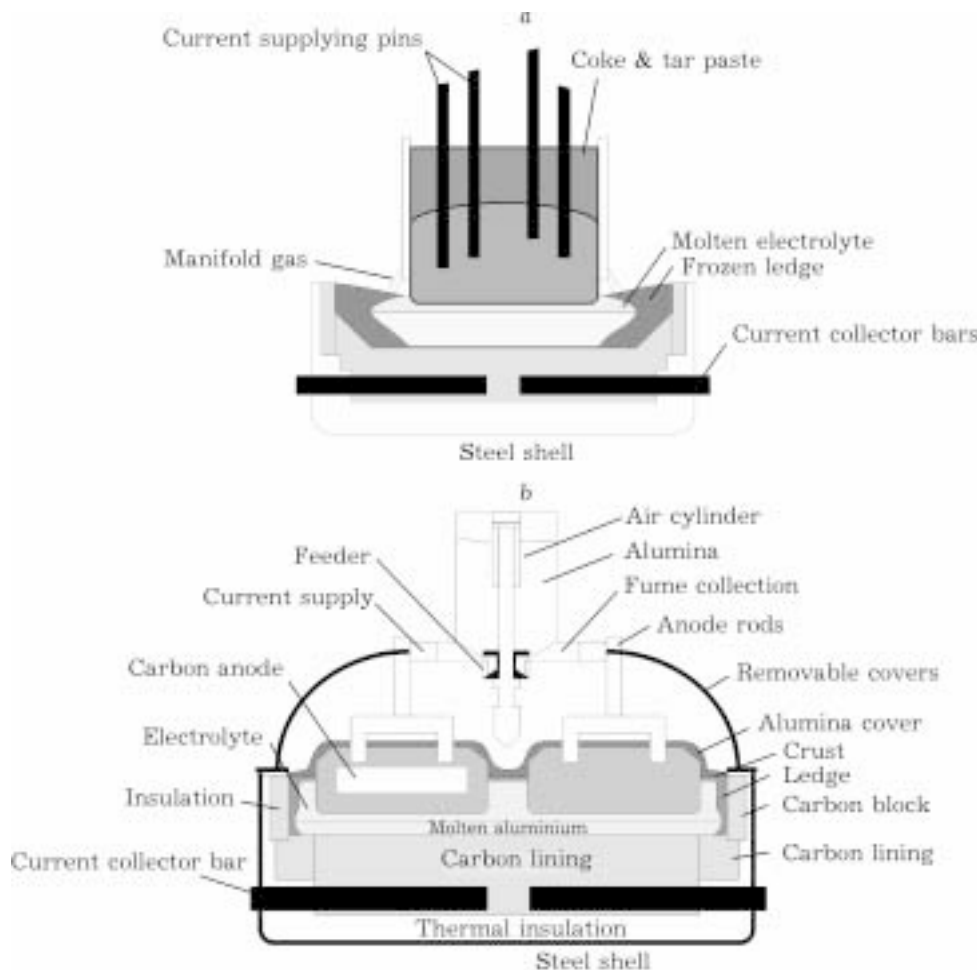

Fig. 3. The aluminium industry switched over from Soderberg (top) (*a*) to pre-baked (*b*) electrodes (bottom) to minimize pollution.

developed to treat the dust to recover its zinc values before disposal.

THE ALUMINIUM INDUSTRY

The aluminium industry is based on the leaching of bauxite with sodium hydroxide at high temperature and pressure to recover pure alumina, which is then reduced with carbon in electrolytic cells containing fused sodium aluminium fluoride. Carbon electrodes for electrolytic cells 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 cells as needed. In the second type, called Soderberg electrodes after their inventor, the carbon paste is added periodically into a large casing and the heat released from the 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. The Soderberg electrodes were considered more economical and displaced the pre-baked electrodes. Today, the tendency is reversed, the modern technology is based on pre-baked electrodes although more costly but less polluting at the work place (Fig. 3).

During the production of metallic aluminium, CO and CO_2 are formed as a result of the electrolytic reduction of Al_2O_3 by the carbon electrodes. These gases are generally not considered harmful to the environment because CO is usually burned to CO_2 before leaving the stacks. However, they always contain a small amount of fluorine compounds. The fluorine emission from this source was about 3 mln t per year. The source of this fluorine is the fused electrolyte in the cells. Modern reduction plants have not only solved this problem but also recovered the major part of fluorine by sorbing it on the Al_2O_3 entering the cell.

TREATMENT OF SULPHIDE ORES

During the recovery of copper, nickel, lead, and zinc from their sulphide ores, SO_2 is formed in large quantities. The problem associated with this gas is twofold:

• About 30 % of this gas are actually utilized to make H_2SO_4 and the rest is emitted in the atmosphere because its concentration in the exit gases is too low to be utilized for making acid when a reverberatory furnace is used. Millions of tons of SO_2 from this source are emitted annually in the environment.

• Sulphide ores normally contain small amounts of mercury, arsenic, selenium, and tellurium. These impurities either go to the process gases used to make H_2SO_4, 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.

Recovery or disposal of SO_2

Processes aimed at solving the problem of SO_2 in smelter gases by obtaining highly concentrated SO_2 suitable for liquefaction, or exit gases rich in SO_2 that are suitable for H_2SO_4 manufacture, must assume the existence of a nearby market. Because of the urgency of the problem, it has been even considered to change existing technology and to seek for new processes in which SO_2 is not a reaction product. Processes yielding elemental sulphur would be ideal because sulphur is easy to store, cheap to transport, and can be converted to SO_2 or H_2SO_4 readily when need arises. In this respect hydrometallurgy offers a promising approach. Most reverberatory furnaces, which are responsible for a great part of SO_2 emissions, have been replaced by flash smelting furnaces, which produce SO_2 in concentrations suitable for sulphuric acid manufacture.

Elimination of metallic impurities from smelter gases

An appreciable amount of As, Se, and Te is volatilized during the treatment of sulphide ores and most of these are collected in the dust recovery system. But mercury that is also volatilized and is present in the exit gases is not removed by such a system because of its much lower concentration. Processes have been developed to cope with this problem and they

are now widely adopted. The following can be mentioned.

The Outokumpu Process. In this process SO_2 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 H_2SO_4 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 sulphate. The acid is recycled and when it becomes saturated in $HgSO_4$, the crystals are separated in thickeners.

The Odda Process. This process is based on the scrubbing of the gases by a solution of mercuric chloride. Mercury in the gases will react forming mercurous chloride which is precipitated and filtered.

Aqueous oxidation

The pyrometallurgical route for treating sulphide concentrates was the logical way because historically this was the only way known. When, however, hydrometallurgical knowledge became well established, it became evident recently that other routes are possible based on the formation of elemental sulphur, thus avoiding the SO_2 problem. Under certain leaching conditions (temperatures about 150 °C, in an acid medium, and under oxidizing atmosphere) elemental sulphur can be produced directly in one step (Fig. 4). The zinc industry
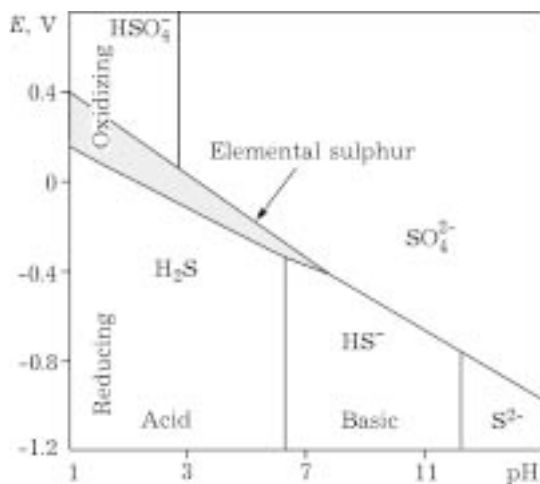
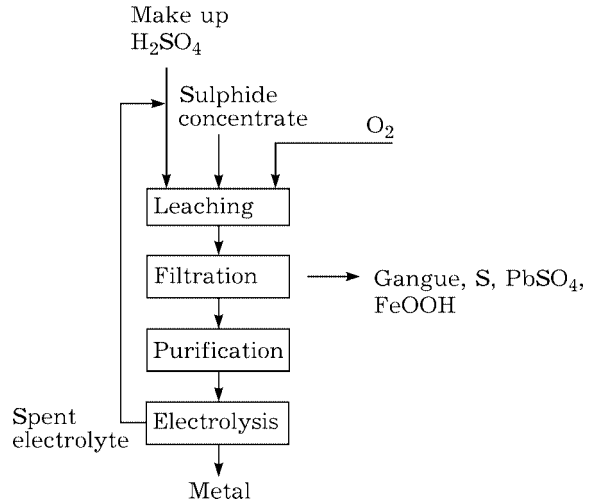Fig. 4. Formation of elemental sulphur during aqueous oxidation of sulphides.

Fig. 5. Aqueous oxidation-electrowinning of sulphide concentrate.

was the first and the only one so far to adopt such technology. Before World War I zinc was produced exclusively by the retort processes, which were highly polluting and energy intensive. This was replaced by the roasting-leaching-electrowinning route. This new technology, however, introduced serious disposal problems. Finally the pressure leaching technology was introduced in the 1980s whereby elemental sulphur was produced, instead of SO_2, according to the reaction:

$$ZnS + 2H^+ + 1/2O_2 \rightarrow Zn^{2+} + S + H_2O$$
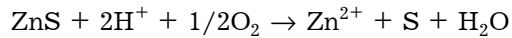
The process is self-sufficient with respect to acid consumption since the zinc-containing solution can be electrolyzed by the standard technology to generate the acid needed for leaching (Fig. 5). Elemental sulhur can be stock piled to be used when needed to make H_2SO_4 or shipped long distances to the market. Oxygen is preferred to other oxidizing agents, *e. g.*, Fe^{3+} ion, HNO_3, *etc.*, because it does not need to be regenerated. The same technology can be applied to other sulphide concentrates.

In case of chalcopyrite the process is also self-sufficient with respect to the acid used when the copper-containing solution is electrolyzed or precipitated by hydrogen under pressure:
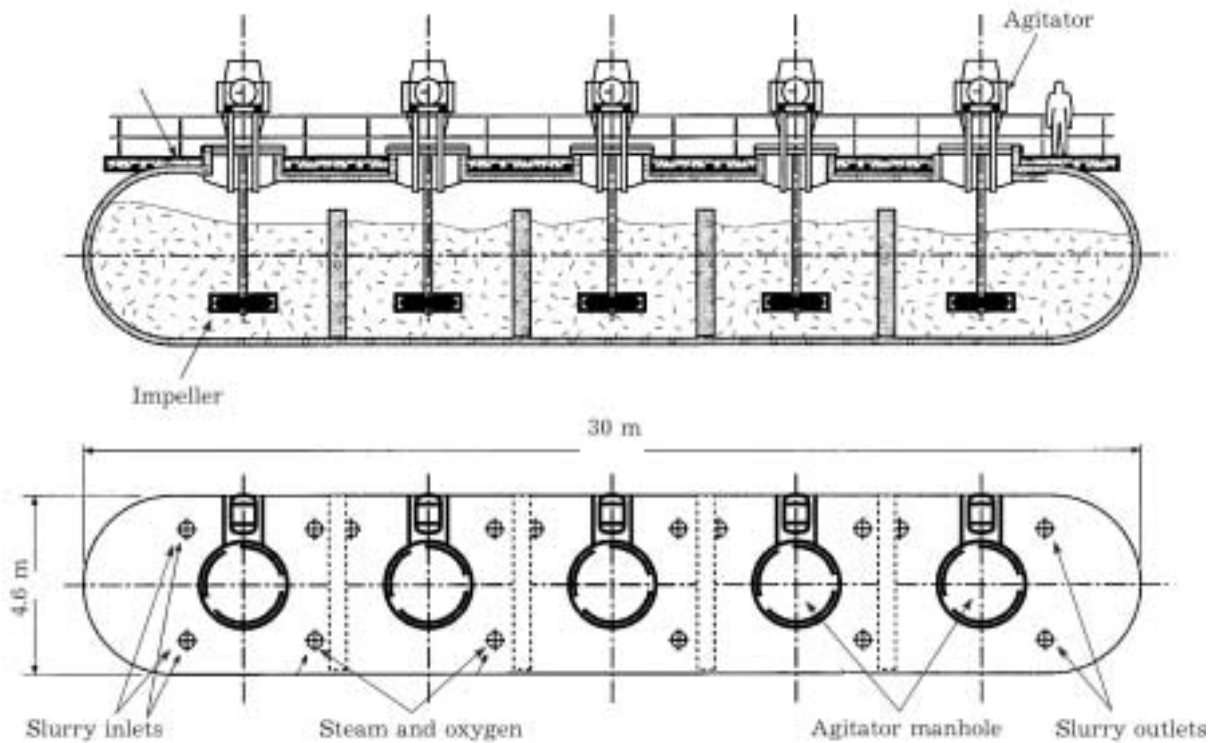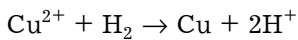
$$2CuFeS_2 + 4H^+ + 5/2O_2 \rightarrow 2Cu^{2+} + 2FeOOH + 4S + H_2O$$

$$Cu^{2+} + H_2O \rightarrow Cu + 2H^+ + 1/2O_2$$
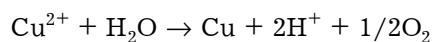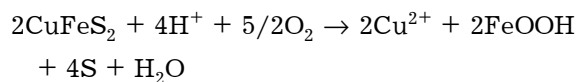
Fig. 6. Horizontal autoclave for treating concentrates.

$$Cu^{2+} + H_2 \rightarrow Cu + 2H^+$$

Initially autoclaves were used for leaching bauxites more than 100 years ago, were applied for leaching laterites in 1940s but the technology has progressed extensively since the mid 1980s when applied for zinc sulphide concentrates and refractory sulphide gold bearing ores. There are presently four plants treating zinc sulphide concentrates with elemental sulphur recovery, 23 autoclaves operating world wide for refractory gold ores and 10 for laterites. Some of these are 5.6 m internal diameter and about 30 m long, lined with acid-resistant bricks (Fig. 6).

Operational experience in autoclave technology has made rapid progress and the result is much smoother and safer operation. New special alloys have been introduced to reduce maintenance time. Sophisticated instrumentation allows for many safety features. The advanced design has allowed for greater availability and as a result, operating and maintenance costs have decreased. Many of these autoclaves operate up to 9 months continuously without shutdown. Large and efficient membrane piston pumps that can feed autoclaves continuously are now available. Flash tanks for heat recovery from the discharged slurry are widely used for efficient operation.

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