# CONTROL OF POLLUTION IN THE NON-FERROUS METALS INDUSTRY

**V. Beschkov**

*Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

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**Contents**

**Summary**

This chapter is concerned with the practical use of non-ferrous metals which is well known from the ancient times. It discusses modern technical progress that is associated with bigger amounts of these metals, mainly copper, aluminum, lead and zinc, used for various purposes in modern society. Their extended demand and production imposes severe problems on environment, directly, at their mining and smelting, and indirectly, by the enhanced energy demand. Therefore environmental problems in non-ferrous metals manufacturing are quite similar to those in other branches of modern industry. In the present review the mostly used technologies for production of the mentioned non-ferrous metals are discussed. Attention is paid to the secondary metals recovery as an issue for mitigation of the impact on environment, exerted by the primary metal production. The environmental issues of these technologies, as emissions in air, wastewater treatment and chemicals recycling are considered.

**1. Introduction**

The most widely and substantially used non-ferrous metals in human civilization are copper, lead, zinc and aluminum. Their massive distribution reflects on their strong impact on environment, either during their recovery, or during their use in household and human practice. There are many other metals achieving great importance in modern civilization, like nickel, cadmium, some transient elements, like germanium, and some precious metals (gold, silver, platinum, etc.) However, the bulk of their production cannot be compared to that of copper, lead, zinc, and aluminum. This fact makes it clear, why the impact on environment of these metals production is so strong, starting with mining and dressing and ending with smelting.

Besides aluminum, the rest of considered metals are manufactured from their sulfide ores. Since the metal content in these ores is less than 2-3 per cent, it is clear that extraction of sulfide components from the total rocky mass is associated with extensive mining effort and enormous amount of waste release. The next steps are associated with reductive processes in pyrometallurgy. It means, that too much energy is required, associated with air pollution from power generation and emissions of particulate and sulfur dioxide from sulfide roasting.

Waste minimization and energy saving are the most frequent approaches to environment protection in the non-ferrous metal industries. One of the methods to save raw materials and thus to facilitate mining activities is the reuse of used metal articles.

The technologies for these four metals production will be considered in the following, together with their environmental issues.

**2. Production of Aluminum**

**2.1. Process Technology**

All of the methods applied to aluminum production are based on electrolysis of molten alumina. The first step is generally associated with the preparation of pure enough alumina from bauxite by the Bayer process. The latter consists in selective separation of

alumina and its hydrates from the mineral by extraction with sodium hydroxide:

$Al_2O_3 .x(H_2O) + 2NaOH = 2NaAlO_2 + (1+x)(H_2O)$
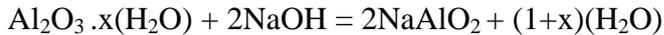
This process is carried out in digesters, under high pressure and high temperatures. Then alumina is practically separated from silicon, iron, titanium and calcium oxides as insoluble components in the solid waste residue.

Alumina is then precipitated from sodium aluminate solution, cooling by flash evaporation, thus producing steam and utilizing the heat for initial slurry heating. The next process is clarification of the obtained solution in hydrocyclons (for coarse particles). Starch promotes agglomeration and settling of fine particles in a clarifier. The overflow is then filtered to remove any remaining suspended solids. The clarifier underflow is washed in a thickener to remove as much caustic as possible before being sent to the residue pond.

The filtrate containing sodium aluminate is precipitated at $120^0C$ to aluminum hydroxide:

$2NaAlO_2 + 4H_2O = 2Al(OH)_3 . + 2NaOH$
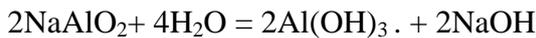
After precipitation, the slurry containing tri-hydrate crystals is sent to classification, (separation according to the crystal size). The coarse product is washed to remove the excess sodium hydroxide, dewatered on vacuum filters, and sent to calcination. The finer crystals are recycled to the precipitator as seed, providing nucleation sites for precipitation to occur. Spent liquor from the precipitators is recycled to the digesters.

The next step is alumina calcination. It is accomplished in rotary kilns or fluidized-bed furnaces at about $1000^0C$.

In the second step electrolysis of the molten alumina takes place. It is carried out in a semi-batch way in large rectangular electrolytic cells called pots with dc input of up to 280 000 A at about 5 volts. The pot is lined with a refractory insulating shell on which carbon blocks are placed to form the cathode. Steel collector bars are inserted at the bottom to collect current from the pot. The insulation is designed to allow enough heat loss at the vertical walls so that a protective layer of frozen electrolyte can form, but not at the bottom, where electrical conductivity must be maintained between the molten aluminum and the cathode block.

Electrolysis of the molten bath involves several complex electrode reactions. The overall reaction is the reduction of alumina with carbon, forming carbon dioxide with the released oxygen:

$Al_2O_3 + 3/2C = 2Al + 3/2CO_2$
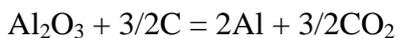
In order to attain sufficient ion mobility alumina is mixed with molten cryolite ($Na_3AlF_6$, melting point: $1006^0C$). It is placed in the cavity between the cathode blocks, and anodes, also of carbon, which are immersed in the cryolite, completing the electrical path. Alumina is fed intermittently to the pot in its central part, after punching and breaking the crust of frozen electrolyte. Aluminum is tapped once a day, after

reaching a certain level. A big share of the electric energy is spent to maintain the high temperature. However, addition of some quantity of calcium fluoride and/or aluminum fluoride reduces the melting point with 4-5$^0$C for each fraction added. Hence, electrolysis could be accomplished at 950$^0$C with a considerable saving of energy.

The practical scheme of aluminum production is shown in Figure 1.
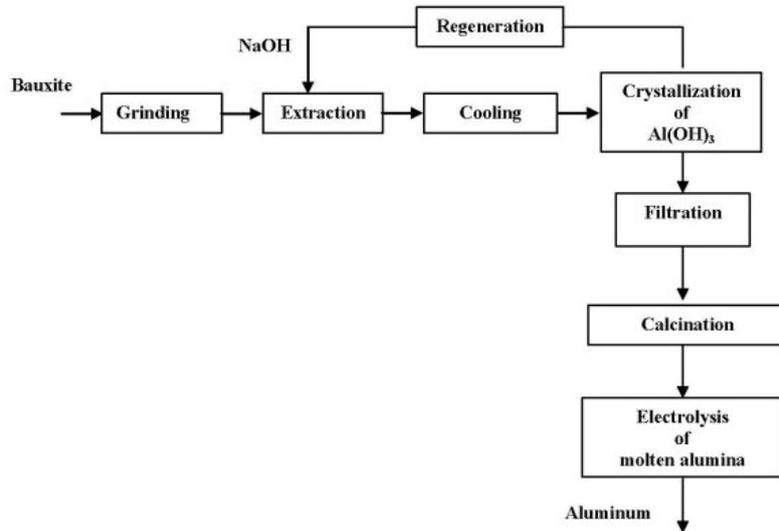


Figure 1: Principal scheme of aluminum production according to Bayer process

The preparation and the use of electrodes, particularly the anodes, are a very important feature of aluminum production. As the anodes are consumed by combining with oxygen from the alumina, they are lowered in the bath and replaced when most of the carbon is gone. After removal of the spent anode, the latter is mechanically cleaned from the adhered bath and used for preparation of new ones.

In the Soderberg cells, continuous self-baking anodes are used instead of pre-baked ones. A paste, consisting of coal tar pitch and petroleum coke is fed to the top of a steel casing and is baked into an anode by heat from the cells and heat, generated by the current passing through the anode. As the lower portion of the anode is consumed, the mass of baked material moves downward through the casing. Then more paste is added to the top, and so forth.

## 2.2. Emissions Control

### 2.2.1. Emissions in the Air

Emissions of particulate take place at the step of bauxite preparation for extraction of alumina, because of crushing and grinding in ball mills, and when necessary, drying in rotary kilns. Mechanical collectors, like cyclones are followed by scrubbers or electrostatic precipitators.

The flue gases resulting from calcination contain alumina and cyclone separators followed by electrostatic precipitators control water vapor. Hence, additional amounts of alumina may be recovered.

During the electrolysis the main gaseous emissions besides carbon dioxide (formed from the oxygen released on the anode and the carbon electrode) are gases, containing hydrogen fluoride, sulfur dioxide, carbon monoxide, hexafluorethane, and carbon tetrafluoride (formed from the carbon electrodes and the fluoride additives). Hydrogen fluoride is formed from the fluoride compounds hydrolyzed by the adsorbed water and hydration water of alumina, and from the hydrogen in the anodes. Air blasting enhances this release. The fluorides are extremely severe pollutants of the environment, threatening the life of plants and animals.

Particulate emissions of fluoride result from vaporization of fluorine compounds from the molten bath and subsequent condensation in the cooler zone of the pot. Sulfur dioxide comes from the sulfur present in the coke and the coal tar pitch binder in the anodes. The transportation and handling of the materials are also sources of pollution.

Besides, other sulfur and carbon containing compounds are released, carbonyl sulfide, carbon disulfide, as well as aromatic hydrocarbons. They could be captured in a scrubber or combusted. Gaseous emissions from all electrolysis cells could be collected by hooding in a common duct and passed through a big stack, where the primary purification system is placed.

For bigger plants such a system is not sufficient. Therefore, liquid scrubbing for fluorides removal is required. After the scrubbers electrostatic precipitators (98-99 per cent efficiency) are placed. Thus fluorides and aerosols are removed from the waste gases. Next, absorption columns with sieve trays are proposed, because they combine the scrubbing process with the particulate removal as it is in the electrostatic precipitators.

In the last 20 years there are systems that use dry removal of fluorides, using γ-alumina as adsorbent. Two types of dry systems are used: the fluidized-bed ones where the off-gases force the alumina particles into a fluidized state, and, systems where alumina is injected in a zone of high gas velocity and turbulence. These dry scrubbing systems are capable of removing over 99 per cent of HF. The adsorbed fluorides react with the alumina to yield $AlF_3$, which could be recycled in the electrolytic process. With this high recovery and reusing abilities, consumption of fluoride has been reduced significantly in smelters with dry scrubbing systems. Therefore, the emissions from the stacks of the facilities with dry systems for control contribute very little to the overall plant fluoride emission.

The purpose of the secondary systems of emissions control is to reduce the release of particulate and gaseous pollutants in equipment with not enough efficient primary systems. In the secondary systems gas flow rates are too high and therefore their size is extremely large. Thus the prices of secondary systems are too high and the required effects are not commensurate. Therefore, efforts must be focused on improvement of the operating conditions for the primary systems. Some of them consist in combinations of

wet and dry fluorides removal, introduction of more efficient filters for particulate, etc.

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**Biographical Sketch**

**Venko N. Beschkov** was born in 1946 in Sofia, Bulgaria. He obtained his M. Sc. degree in inorganic and physical chemistry in the University of Sofia "St. Clement Ohridski" (1969). He obtained his Ph.D. degree in the Central Laboratory of Chemical Engineering at the Bulgarian Academy of Sciences in Sofia Bulgaria (1978), and his D.Sc. degree in 1996. He was promoted as associate professor in 1984 and as a full professor in 1997. He is Director of Institute of Chemical Engineering at the Bulgarian Academy of Sciences (since 1993).

The scope of his scientific activity is on mass transfer operations in chemical and biochemical engineering, bioprocess engineering and environment protection (fine chemicals production, waste water treatment, gas pollution removal, etc.). He has over 60 scientific papers and 1 monograph (*Boyadjiev Chr., V.Beschkov, Mass Transfer in Liquid Film Flow, Publishing House of the Bulgarian Academy of Sciences, Sofia, 1984*) published. He is an editor-in-chief of the scientific journal *Bulgarian Chemical Communications* (since 1996). He was also an editor of textbooks on chemical technology in Bulgarian (1986).

His teaching activity consisted in delivering courses in hydrodynamics in the Faculty of Chemistry, University of Sofia "Climent Ohridski" as a assistant professor and a reader (1976-1984); in biochemical engineering in the Faculty of Biology, University of Sofia "Climent Ohridski" as a reader (1987-1989); in technology in bioconversion as a reader in the University of Chemical Technology & Metallurgy, Sofia, Bulgaria (since 1999).

He was Deputy-minister of The Ministry of Environment Protection in the Government of The Republic of Bulgaria (1991/92), consultant and trainer in different international projects on environment protection (since 1993).