**SNAP CODE:** **030309**

**SOURCE ACTIVITY TITLE:** **PROCESSES WITH CONTACT**
***Secondary Copper Production***

**NOSE CODE:** **104.12.10**

**NFR CODE:** **1 A 2 b**

**ISIC:** **2420**

## 1 ACTIVITIES INCLUDED

This chapter includes information on atmospheric emissions during the production of copper in secondary copper smelters. Secondary copper smelters produce about 40 % of the total copper production in the world (e.g. Pacyna, 1989). Pyrometallurgical processes are used to rework scrap and other secondary materials. As with primary copper production, final refining, where practised, is electrolytic. This chapter describes the methods to estimate emissions of atmospheric pollutants during the secondary copper recovery (e.g. Parker, 1978; UN ECE, 1994).

## 2 CONTRIBUTIONS TO TOTAL EMISSIONS

There are several trace elements which can be emitted during the secondary copper production. However, these emissions are not very significant on a global scale. Nriagu and Pacyna (1988) concluded that the secondary copper production contributes well below 1 % of the total atmospheric emissions of copper, lead, antimony, selenium, and zinc. Similar contribution of atmospheric emissions during the secondary copper production was estimated for the European emissions in the beginning of the 1980’s (Pacyna, 1983). However, a secondary copper smelter or refinery can be an important emission source of trace element contamination on a local scale.

The contribution of emissions released from secondary copper production to total emissions in countries of the CORINAIR90 inventory is given as follows:

**Table 2.1: Contribution to total emissions of the CORINAIR90 inventory** (*28 countries*)

| Source-activity | SNAP-code | Contribution to total emissions [%] | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Secondary Copper Production | 030309 | $SO_2$ | $NO_x$ | NMVOC | $CH_4$ | CO | $CO_2$ | $N_2O$ | $NH_3$ | TSP* | $PM_{10}$* | $PM_{2.5}$* |
| Typical contribution | | 0 | - | 0 | - | 0 | - | - | - | 0.059 | 0.103 | 0.113 |
| Highest value | | | | | | | | | | 0.171 | 0.287 | 0.350 |
| Lowest value | | | | | | | | | | 0.000 | 0.000 | 0.000 |

* EU $PM_{2.5}$ Inventory project for EU25 for the year 2000 (TNO, 2006), contribution to total national emissions, excluding agricultural soils
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

# 3 GENERAL

## 3.1 Description

A secondary copper smelter is defined as any plant or factory in which copper-bearing scrap or copper-bearing materials, other than copper-bearing concentrates (ores) derived from a mining operation, is processed by metallurgical or chemical process into refined copper and copper powder (a premium product).

The recycling of copper is the most comprehensive among the non-ferrous metals. The copper metal scrap can be in the form of:

- copper scrap, such as fabrication rejects, wire scrap, plumbing scrap, apparatus, electrical systems, products from cable processing,
- alloy scrap, such as brass, gunmetal, bronze, in the form of radiators, fittings, machine parts, turnings, shreddar metals, and
- copper-iron scrap like electric motors or parts thereof, plated scrap, circuit elements and switchboard units, telephone scrap, transformers, and shreddar materials.

Another large group of copper-containing materials is composed of oxidised materials, including drosses, ashes, slags, scales, ball mill fines, catalysts as well as materials resulting from pollution control systems.

The copper content of scrap varies from 10 to nearly 100% (UN ECE, 1994). The associated metals which have to be removed are mainly zinc, lead, tin, iron, nickel and aluminium as well as certain amounts of precious metals.

Depending on their chemical composition, the raw materials of a secondary copper smelter are processed in different types of furnaces, including:

- blast furnaces (up to 30% of Cu in the average charge),
- converters (about 75% Cu), and
- anode furnaces (about 95% Cu).

The blast furnace metal (“black copper”) is treated in a converter, the converter metal is refined in an anode furnace. In each step additional raw material with corresponding copper content is added.

In the blast furnace , a mixture of raw materials, iron scrap, limestone and sand as well as coke is charged at the top. Air which can be enriched with oxygen is blown through the tuyeres, the coke is burnt and the charge materials are smelted under reducing conditions. Black copper and slag are discharged from tapholes.

The converters used in primary copper smelting, working on mattes containing iron sulfide, generate surplus heat and additions of scrap copper are often used to control temperature. The converter provides a convenient and cheap form of scrap treatment, but often with only moderately efficient gas cleaning. Alternatively, hydrometallurgical treatment of scrap, using ammonia leaching, yields to solutions which can be reduced by hydrogen to obtain copper powder (e.g. Barbour et al., 1978). Alternatively, these solutions can be treated by solvent extraction to produce feed to a copper-winning cell.

Converter copper is charged together with copper raw materials in anode furnace operation. For smelting the charge, oil or coal dust is used , mainly in reverberatory furnaces. After smelting, air is blown on the bath to oxidise the remaining impurities.

Leaded brasses, containing as much as 3% of lead, are widely used in various applications and recycling of their scrap waste is an important activity. Such scrap contains usually much swarf and turnings coated with lubricant and cutting oils. Copper-containing cables and motors contain plastic or rubber insulants, varnishes, and lacquers. In such cases, scrap needs pre-treatment to remove these non-metallics. The smaller sizes of scrap can be pre-treated termally in a rotary kiln provided with an after-burner to consume smoke and oil vapors (so-called Intal process). There are also various techniques available to remove rubber and plastic insulations of cables (e.g. Barbour et al., 1978; UN ECE, 1994).

Atmospheric emissions of various pollutants are generated during all three types of processes employed in the secondary copper industry.

## 3.2 Definitions

Secondary copper production: - production of copper from materials other than ores.

## 3.3 Controls

Controls in secondary copper production should include effective dust collecting arrangements for dust from both primary exhaust gases and fugitive dust emissions. Fabric filters can be used reducing the dust emissions to below 10 mg/ $m^3$ (UN ECE, 1994).

# 4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers :

- Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.
- Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.
- Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the simpler methodology (equivalent to Tiers 1 and 2), where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment.

Consequently the simplified methodology is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = AR \times EF$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

Default emission factors for this purpose are provided in Section 8. However, it should be noted that the chemical composition of input scrap is one of the most important factors affecting the amount of emissions. The chemical composition of input scrap varies considerably from one plant to another and so do emission factors.

# 5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3), to estimate emissions of gaseous pollutants from the secondary copper production is based on measurements or estimations using plant specific emission factors. Guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

## 6 RELEVANT ACTIVITY STATISTICS

Information on the production of copper in secondary smelters, suitable for estimating emissions using of the simpler estimation methodology (Tier 1 and 2), is widely available from UN statistical yearbooks or national statistics.

The detailed methodology (Tier 3) requires more detailed information. For example, the quantities of the metal produced by various types of industrial technologies employed in the cement industry at plant level. This data is however not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 2.2.1.3 " Choice of activity statistics".

## 7 POINT SOURCE CRITERIA

Secondary copper smelters should be regarded as point sources if plant specific data are available.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 8.1 contains fuel related emission factors for secondary copper production based on CORINAIR90 data [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product, $g/m^3$), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 38.5 up to 100 GJ/Mg product has been reported.

## Table 8.1: Emission factors for secondary copper production[7)]

| | | Type of fuel | NAPFUE code | Emission factors $SO_2$[2)] [g/GJ] | $NO_x$[3)] [g/GJ] | NMVOC[4)] [g/GJ] | $CH_4$ [g/GJ] | CO [g/GJ] | $CO_2$ [kg/GJ] | $N_2O$ [g/GJ] |
|---|---|---|---|---|---|---|---|---|---|---|
| l | oil | residual | 203 | 495-1,470[1)] | 150[1)] | 30[1)] | 30[1)] | 15[1)] | 76-78[1)] | 2[2)] |
| l | oil | gas | 204 | 94-1,410[1)] | 100[1)] | 1.5[1)] | 1.5[1)] | 12[1)] | 73-74[1)] | 2[1)] |
| g | gas | natural | 301 | 0.28[1)] | 100[1)] | 4[1)] | 4[1)] | 13[1)] | 57[1)], 60[5)], 59[6)] | 1[1)] |
| g | gas | liquified petroleum gas | 303 | 0.04[1)] | 100[1)] | 2.1[1)] | 0.9[1)] | 13[1)] | 65[1)] | 1[1)] |

1) CORINAIR90 data, point sources

| | | | | |
|---|---|---|---|---|
| 2) | $SO_x$: (EPA, 1990) | 750 | g/Mg charged | Scrap dryer (rotary) |
| | | 6,400 | g/Mg charged | Wire burning, incinerator |
| | | 250 | g/Mg charged | Crucible and pot furnace, charged with brass and bronze |
| | | 15 | g/Mg charged | Electric arc furnace, charged with brass and bronze |
| | | 15 | g/Mg charged | Electric induction furnace, charged with brass and bronze |
| | | 2,182 | g/Mg product | Refining |
| | | 17,209 · S | g/m³ fuel | Secondary metal production, process heaters NAPFUE 204, S = sulphur content of fuel |
| | | 19,006 · S | g/m³ fuel | Secondary metal production, process heaters NAPFUE 203, S = sulphur content of fuel |
| 3) | $NO_x$: (EPA, 1990) | 850 | g/Mg charged | Wire burning, incinerator |
| | | 40 | g/Mg charged | Reverberatory furnace, charged with brass and bronze |
| | | 300 | g/mg charged | Rotary furnace, charged with brass and bronze |
| | | 2,397 | g/m³ fuel | Secondary metal production, process heaters, NAPFUE 204 |
| | | 6,591 | g/m³ fuel | Secondary metal production, process heaters, NAPFUE 203 |
| 4) | VOC: (EPA, 1990) | 2 | g/Mg charged | Scrap dryer (rotary) |
| | | 300 | g/Mg charged | Wire burning, incinerator |
| | | 60 | g/Mg charged | Sweating furnace |
| | | 223,500 | g/Mg coke free charge | Cupola, charged with insulated copper or brass and scrap copper |
| | | 90 | g/Mg charged | Cupola, charged with scrap copper or brass and scrap copper |
| | | 2,600 | g/Mg charged | Reverberatory furnace, charged with copper / charged with brass and bronze |
| | | 1,200 | g/Mg charged | Rotary furnace, charged with brass and bronze |
| | | 3,350 | g/Mg charged | Crucible and pot furnace, charged with brass and bronze |
| | | 1,950 | g/Mg charged | Electric arc furnace, charged with copper |
| | | 0 | g/Mg charged | Electric arc furnace, charged with brass and bronze |
| | | 0 | g/Mg charged | Electric induction furnace, charged with copper or brass and bronze |
| | | 24 | g/m³ fuel | Secondary metal production, process heaters, NAPFUE 204 |
| | | 34 | g/m³ fuel | Secondary metal production, process heaters, NAPFUE 203 |
| | | 44,851 | g/Mm³ fuel | Secondary metal production, process heaters, NAPFUE 301 |

5) $CO_2$: Locally contaminated scrap input, brass production (Bremmer, 1995)
6) $CO_2$: Strongly contaminated scrap input, brass production (Bremmer, 1995)
7) It is assumed, that emission factors cited within the table are related to combustion sources in secondary copper production. Footnotes may contain emission factors for total emissions (fuel and process related).

A list of emission factors for several trace elements emitted from secondary copper smelters is presented in Table 8.2. Results of measurements and estimates carried out in various countries are presented. However, in some cases the factors originate from the same sources.

Information available from the above mentioned measurements and estimates does not allow for further differentiation of emission factors with respect to neither various industrial processes involved in the secondary copper production or different production technologies used at present. Therefore, the factors in Table 8.2 can only be used in a simpler emission estimation methodology.

**Table 8.2: Compilation of emission factors for secondary copper production (in g/tonne Cu produced)**

| Element | Estimates by Pacyna (1986) | Estimates in Canada (Jacques, 1987) | PARCOM program (PARCOM, 1992) | Estimates in the U.K. (Leech, 1993) | Estimates in Austria (Schneider, 1994) | Suggested |
|---|---|---|---|---|---|---|
| Arsenic | | | | | 2 | 2 |
| Antimony | 3 | | | | | 3 |
| Cadmium | 4 | | 5 | 5 | 2 | 2-4 |
| Copper | 150 | 200-400 | | | 20 | 20-150 |
| Lead | 50-200 | 230 | 130 | 130 | 50 | 50-130 |
| Nickel | | 1 | | | | 1 |
| Zinc | 500-1600 | | 500 | 500 | 250 | 250-500 |
| Control | ESP, ca. 99% efficiency | Based on question-naires. Most plants use ESPs with 99% efficiency | Unspecified | Based on emission factors by Pacyna and PARCOM | Unspecified | Common ESPs with 99% efficiency |

General emission factors for particulate matter for secondary copper production (all processes, CEPMEIP) are:

TSP: 1 g/kg secondary copper

$PM_{10}$: 0,8 g/kg secondary copper

$PM_{2.5}$: 0,6 g/kg secondary copper

The uncertainty factor in all emission factors is 10 (95% confidence)

Note: The lower limit of the uncertainty range can be found by dividing the emission factor by the uncertainty factor, whereas the upper limit of the uncertainty range can be found by multiplying the range with the uncertainty factor. Example: The emission factor for PM2.5 with an uncertainty range of 10 will therefore be 0,6 gram per kg secondary cupper with an uncertainty range of 0.06 (0.6/10) to 6 (0.6x10).

## 9 SPECIES PROFILES

At present no reliable information exist on physical and chemical species of trace elements emitted during the secondary copper production. It can be assumed that the majority of trace elements volatilized from scrap and other copper-containing materials enter the atmosphere on fine particles.

## 10 UNCERTAINTY ESTIMATES

It is difficult to assess current uncertainties of emission estimates for pollutants emitted during the secondary copper production. Recently it was concluded that up to 50 % of uncertainties can be assigned for the emission estimates of most of the trace elements emitted from major point sources in Europe (Pacyna, 1994). Even bigger uncertainty can be assigned for emission estimates of these compounds from the secondary copper production. Information on emission factors and statistics is more limited for the secondary copper smelters than for major point sources, such as primary smelters and power plants.

## 11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for the secondary copper production. This improvement should focus on preparing individual emission factors for major industrial technologies currently employed in the copper industry. In this way, a detailed methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data on the production of copper in various secondary copper furnaces.

## 12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not applicable.

## 13 TEMPORAL DISAGGREGATION CRITERIA

The secondary copper production is a continuous process. No temporal disaggregation is needed.

## 14 ADDITIONAL COMMENTS

No additional comments.

## 15 SUPPLEMENTARY DOCUMENTS

The following supplementary document can be suggested:
UN ECE State-of-the-Art Report on the Heavy Metals Emissions, the UN ECE Task Force on Heavy Metals Emissions, Prague, the Czech Republic, June 1994.

## 16 VERIFICATION PROCEDURES

At present no specific verification procedures are available for estimation of atmospheric emissions from the secondary copper production. Estimated emission factors could be best verified by measurements at plants using different industrial technologies.

## 17 REFERENCES

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## 18 BIBLIOGRAPHY

No additional documents.

## 19 RELEASE VERSION, DATE AND SOURCE

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Source : Jozef M Pacyna
Norwegian Institute for Air Research (NILU)
Norway

Supported by: Otto Rentz, Dagmar Oertel
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Updated with emission factors (CEPMEIP) for particulates by:
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## 20 POINT OF ENQUIRY

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