PROCESSES WITH CONTACT Primary Lead Production

030304

SOURCE ACTIVITY TITLE:

NOSE CODE:

NFR CODE:

1 ACTIVITIES INCLUDED

The primary lead production process is defined as the production of lead from lead concentrates. A detailed description of other process steps e.g. sintering can be found in chapter B331. However, in the following if useful for description sintering processes are included.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of gaseous emissions released from primary lead production to total emissions in countries of the CORINAIR90 inventory is given as follows:

| Table 2.1: Contribution to total emissions of the COF | RINAIR90 inventory (28 countries) |
|---|--|
|---|--|

| Source-activity | SNAP-code | Contribution to total emissions [%] | | | | | | | |
|-------------------------|-----------|-------------------------------------|-----------------|-------|--------|----|--------|--------|-----------------|
| | | SO_2 | NO _x | NMVOC | CH_4 | CO | CO_2 | N_2O | NH ₃ |
| Primary Lead Production | 030304 | 0.2 | 0 | - | - | 0 | 0 | - | - |

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

The contribution of heavy metal emissions from primary lead production to the total heavy metal emissions, according to IWAD [7], is given in Table 2.2.

Table 2.2. The contribution of heavy metal emissions from primary lead production to
the total emissions of the IWAD study [7]

| Contribution to total emissions (%) | | | | | | | |
|-------------------------------------|----|-----|----|-----|-----|--|--|
| Cd | Cr | Cu | Ni | Pb | Zn | | |
| 1.1 | 0 | 0.2 | 0 | 1.5 | 0.3 | | |

0 = emissions are reported, but the exact value is below the rounding limit

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3 GENERAL

3.1 Description of activities

This process contains the classical steps of ore pretreatment and concentration, sintering, smelting, and product refining. Most primary lead smelters also produce other metals to a certain extent. The process route is based on sintering, reduction of sinter in a shaft furnace, and refining of bullion, either pyrometallurgically or hydrometallurgically.

In the sintering process fine particles of metal ores are agglomerated into nodules, briquettes, sinter, or pellets. Also a roasting process is involved in which lead sulphide is converted into lead oxide. Dust emissions result from handling and stockpiling of raw materials or intermediate products. Abatement methods are the use of bag filters, wet scrubbers or electrofilters.

In the smelting process ore, coke, and flux compounds are heated either in a shaft furnace or an electric furnace. Dust abatement can be provided by bag filters or electrofilters. Improved abatement is encapsulation or evacuation of the process.

The refining process is mainly directed at the removal of copper, silver, zinc, and bismuth. Dust emissions mainly occur at the treatment of the different by-product streams.

Several improved processes are either in the pilot stage, or being used at a single plant. However, no general applicable information is available yet.

3.2 Definitions

| Sintering process | Agglomeration of ore particles, flux compounds and other material by |
|-------------------|---|
| | the combustion of coke. |
| Roasting process | Oxidation of lead concentrate converting the lead sulphide to lead oxide. |

3.3 Techniques

The main techniques for the smelting process are the shaft furnace and the electric furnace process. For refining the main techniques are pyrometallurgical refining and hydrometallurgical refining. Several direct smelting technologies have been under development or are being developed yet. Information about the emissions of these techniques is not yet available.

3.4 Emissions

The main emissions during the primary lead production are dust emissions.

Pollutants released are sulphur oxides (SO_x) , nitrogen oxides (NO_x) , volatile organic compounds (non-methane VOC and methane (CH_4)), carbon monoxide (CO), carbon dioxide (CO_2) , and nitrous oxide (N_2O) . According to CORINAIR90 the main relevant pollutants is SO_2 (see also table 2.1).

The most relevant step with regard to SO_2 emissions is the sintering process (for details see B331). However, only about 7 % of the total sulphur in the ore is emitted as SO_2 . The

remainder is captured by the slag. The concentration of this SO_2 stream can vary from 1.4 to 7.2 g/m³, depending on the amount of dilution air injected to oxidise the carbon monoxide and to cool the stream before baghouse particulate removal [1].

Nearly 85 % of the sulphur present in the lead ore concentrate is eliminated in the sintering operation (see chapter B331). In handling process offgases, either a single weak stream is taken from the machine hood at less than 2 % SO₂, or two streams are taken, a strong stream (5 to 7 % SO₂) from the feed end of the machine and a weak stream (less than 0.5 % SO₂) from the discharge end. Single stream operation has been used if there is little or no market for recovered sulphur, so that the uncontrolled, weak SO₂ stream is emitted to the atmosphere.

When sulphur removal is required, however, dual stream operation is preferred. The strong stream is sent to a sulphuric acid plant, and the weak stream is vented to the atmosphere after removal of particulate [1].

Sulphur oxides are also generated in blast furnaces during the smelting process from small quantities of residual lead sulphide and lead sulphates in the sinter feed. The quantity of these emissions is a function not only of the sinter's residual sulphur content, but also of the sulphur captured by copper and other impurities in the slag [1].

3.5 Controls

The dust emissions can be abated by using fabric filters, wet scrubbers or electrofilters. Improvement can be achieved by using encapsulation or evacuation. New approaches are under development.

The SO₂ containing emissions are often used as input for sulphuric acid plants. Here, emissions from combustion and from other process steps are reconciled. Single stage sulphuric acid plants can attain sulphur oxide levels of 5.7 g/m³, and dual stage plants can attain levels of 1.6 g/m³. Typical efficiencies of dual stage plants in removing sulphur oxides can exceed 99 %. Other technically feasible SO₂ control methods are elemental sulphur recovery plants and dimethylamine and ammonia absorption processes [1].

4 SIMPLER METHODOLOGY

An approach calculating the emissions from economic or production statistics is feasible. Emission factors are presented in section 8.

5 DETAILED METHODOLOGY

Information about the newer processes mentioned above is not yet available to allow a more detailed methodology to be followed.

6 RELEVANT ACTIVITY STATISTICS

Lead Production Statistics should be available nationally or from international statistics.

7 POINT SOURCE CRITERIA

The primary lead production should be treated as a point source if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The emissions can vary widely depending on the ore used and the abatement measures applied, see Table 8.1 for reported emission factors. The emission factors given in Table 8.2 were prepared for the PARCOM-ATMOS Emission Factors Manual 1992. The factors for the emissions are based on the information from Table 8.1.

| Table 8.1. | Emission factors for primary lead production (g/Mg product) as reported by |
|-------------------|--|
| | several countries/authors |

| | Swe | den [2] | | Poland [3] | | Germany [4] | Pacyna [5,6] |
|----------|---------|----------|----------|------------|----------|-------------|--------------|
| Compound | limited | improved | limited | improved | unabated | unknown | unknown |
| Arsenic | 3 | 0.2 | 16-43 | - | - | 3 | 300 |
| Cadmium | 3 | 0.6 | 10-22 | - | - | 6 | 10 |
| Copper | 10 | 4 | 10 | 7 | - | - | - |
| Lead | 400 | 200 | 560-1200 | - | - | 400 | 3000 |
| Mercury | - | - | - | - | - | - | 3 |
| Zinc | 50 | 20 | 110 | - | 680 | - | 110 |

| Substance | Emission factor | | | | | | |
|-----------|-----------------|-----------|------------------|--|--|--|--|
| | limited | improved | unknown level of | | | | |
| | abatement | abatement | abatement | | | | |
| Arsenic | 3 | 0.5 | 10 | | | | |
| Cadmium | 10 | 1 | 15 | | | | |
| Copper | 10 | 5 | 10 | | | | |
| Lead | 800 | 200 | 2000 | | | | |
| Mercury | 3 | 3 | 3 | | | | |
| Zinc | 80 | 20 | 100 | | | | |

The following Table 8.3 contains fuel related emission factors for primary lead production based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/m^3) are listed in footnotes. In 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. At this stage no data for the definition of appropriate conversion factors are available.

| | | | | | | | Emission facto | | | | |
|---|------|----|----------------|----------------|--|---|-----------------------|-------------------|---------------------|--|----------------------------|
| | | Ty | pe of fuel | NAPFUE code | SO ₂ ³⁾ [g/GJ] | NO _x ⁴⁾ [g/GJ] | NMVOC⁵) [g/GJ] | CH4 [g/GJ] | CO [g/GJ] | CO ₂ [kg/GJ] | N ₂ O [g/GJ] |
| s | coal | hc | steam | 102 | 149-520 ¹⁾ | 160 ¹⁾ | 15 ¹⁾ | 15 ¹⁾ | 100 ¹⁾ | 94 ¹⁾ , 99 ²⁾ | 4 ¹⁾ |
| s | coal | hc | sub-bituminous | 103 | 838 ²⁾ | 39 ²⁾ | | | | | |
| s | coal | bc | briquettes | 106 | 149-176 ¹⁾ | 140 ¹⁾ | 15 ¹⁾ | 15 ¹⁾ | 100 ¹⁾ | 97 ¹⁾ | 3.5 ¹⁾ |
| s | coke | hc | coke oven | 107 | 149-520 ¹⁾ , 462-501 ²⁾ | 140 ¹⁾ , 35 ²⁾ | 0.5 ¹⁾ | 0.5 ¹⁾ | 100 ¹⁾ | 100-105 ¹⁾ , 105 ²⁾ | 4 ¹⁾ |
| s | coke | bc | coke oven | 108 | 660 ¹⁾ | 200 ¹⁾ | 05 ¹⁾ | 0.5 ¹⁾ | 100 ¹⁾ | 100 ¹⁾ | 4 ¹⁾ |
| 1 | oil | | residual | 203 | 149- 1,470 ¹⁾ | 150-175 ¹⁾ | 4 ¹⁾ | 4 ¹⁾ | 10-15 ¹⁾ | 76-78 ¹⁾ | 2 ¹⁾ |
| 1 | oil | | gas | 204 | 68-1,410 ¹⁾ | 70-100 ¹⁾ | 2.5 ¹⁾ | 2.5 ¹⁾ | 10-12 ¹⁾ | 73-74 ¹⁾ | 2 ¹⁾ |
| g | gas | | natural | 301 | 0.4-149 ¹⁾ , 371 ²⁾ | 50 ¹⁾ , 45 ²⁾ | 2.5 ¹⁾ | 2.5 ¹⁾ | 10 ¹⁾ | 55-56 ¹⁾ , 55 ²⁾ | 1.5 ¹⁾ |

Table 8.3: Emission factors for primary lead production[®]

¹⁾ CORINAIR90 data, area sources (preliminary data)

²⁾ CORINAIR90 data, point sources (preliminary data)

³⁾ SO_x : /1/ 17,209 · S g/m³ fuel: primary metal production, process heaters, NAPFUE 204, S = sulphur content of fuel 19,006 · S g/m³ fuel: primary metal production, process heaters, NAPFUE 203, S = sulphur content of fuel Emission factors of SO₂ given here may contain emissions from combustion of fuel as far as emissions from sintering of ore.

| ⁴⁾ NO _x : /1/ | 2,397 6,591 | g/m³ fuel: g/m³ fuel: | primary metal production, process heaters, NAPFUE 204 primary metal production, process heaters, NAPFUE 203 |
|-------------------------------------|----------------|--------------------------|---|
| ⁵⁾ VOC: /1/ | | g/m³ fuel: g/m³ fuel: | primary metal production, process heaters, NAPFUE 204 primary metal production, process heaters, NAPFUE 203 |

⁶⁾ It is assumed, that emission factors cited within the table are only related to combustion sources in primary lead production (except of SO₂); other process emissions are not covered.

9 SPECIES PROFILES

10 UNCERTAINTY ESTIMATES

The quality class of the emission factors is estimated to be about B.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspects in the current methodology are the emission factors.

The fuel specific emission factors provided in Table 8.3 are related to point sources and area sources without specification. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested to develop emission factors, which include technical or fuel dependent explanations concerning emission factor ranges.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Not applicable if actively treated on a point source basis.

13 TEMPORAL DISAGGREGATION CRITERIA

The primary lead production as such is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

- Richtlinien zur emissionsminderung in nicht-eisen-metall-industrien. Umweltbundesamt 1980.
- US-EPA (ed.): AP 42 CD-Rom; 1994

16 VERIFICATION PROCEDURES

A comparison between the profile of the calculated emissions and the composition of the ore could be used as a verification method.

17 REFERENCES

- 1 EPA (ed.): AIR Facility Subsystem, EPA-Doc. 450/4-90-003, Research Triangle Park, 1990.
- 2 Preliminary note on guidelines on measures and methods for heavy metals emissions control for the primary non-ferrous metal industry in the framework of the ECE task force "Heavy metal emissions" Presented by Sweden on meeting Berlin 21-24 january 1992.
- 3 Heavy metals emission to air in Poland for years 1980-1992, Hlawiczka, S., Zeglin, M., Kosterska, A., Inst. Ecol. Ind. Areas, Report 0-2.081, Katowice, 1995 (in Polish).
- 4 Datenerhebung über die Emissionen Umweltgefärdenden Schwermetalle; Jockel, W., Hartje, J.; Forschungsbericht 91-104 02 588, TüV Rheinland e.V. Köln; 1991.
- 5 Emission factors of atmospheric Cd, Pb and Zn for major source categories in Europe in 1950-1985; Pacyna, J.M.; NILU Report OR 30/91 (ATMOS 9/Info 7); 1990.
- 6 Survey on heavy metal sources and their emission factors for the ECE countries; Pacyna, J.M.; Proc. 2nd Mtg Task Force Heavy Metals Emissions, ECE Convention on Long-range Transboundary Air Pollution Working Group on Technology, Prague, 15-17 October 1991; page 27-55; 1990.
- 7 Calculation of atmospheric deposition of contaminants on the North Sea, Baart, A.C., Berdowski, J.J.M., Jaarsveld, J.A. van, Wulffraat, K.J., TNO-report TNO-MW-R 95/138, 1995.

18 BIBLIOGRAPHY

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20 POINT OF ENQUIRY

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