SNAP CODE: **040103**

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
                                             Sulphur Recovery Plants

NOSE CODE: **105.08.03**

NFR CODE: **1 B 2 a iv**

1   ACTIVITIES INCLUDED

H_2S is a by-product of processing natural gas and refining high sulphur crude oils. Sulphur recovery is the conversion of hydrogen sulphide (H_2S) to elemental sulphur. The Claus process is the most common sulphur recovery process used. Sulphur recovery plants may or may not be located at the processing or refining sites.

If this method is used to estimate emissions from sulphur recovery plants associated with natural gas processing, they should be coded under SNAP code 050301 (chapter B531).

2   CONTRIBUTIONS TO TOTAL EMISSIONS

Emissions from the CORINAIR90 inventory are summarised in table 1.

Table 1:   Contribution to total emissions of the CORINAIR90 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
Sulphur Recovery Plants	040103	0.3	-	0	-	0	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006)[1].

3   GENERAL

3.1   Description

Sulphur recovery, used at both petroleum refineries and natural gas processing plants, converts by-product hydrogen sulphide (H_2S) in sour gas streams to an elemental sulphur product. During initial stages of high-sulphur crude oil or gas processing, process and fuel gases that contain significant amounts of H_2S are treated in a lean amine solution to absorb the sulphide components. The H_2S is subsequently stripped to provide either a feed gas to a

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

sulphur recovery plant or the stripped H_2S may be flared or incinerated at plants where sulphur is not recovered.

In the widely-used multistage Claus sulphur-recovery process, a portion of the H_2S in the feed gas is oxidized to sulphur dioxide (SO_2) and water in a reaction furnace with air or enriched oxygen. After quenching the hot gases to generate steam, the cooler gases are passed through a sulphur condenser to recover liquid sulphur and the gases are reheated. The remaining non-combusted fraction of the feed gas H_2S reacts with SO_2 in catalytic converters (e.g., using aluminium or bauxite catalysts) to form elemental sulphur, water and heat. Since each catalytic stage in the Claus plant recovers only a portion of the incoming sulphur, normally two or more stages are used to achieve up to 97% overall sulphur recovery. Tail gas from the final unit contains a variety of sulphur compounds and normally requires further tail gas cleanup to obtain higher recovery.

3.2   Definitions

3.3   Techniques

See section 3.1.

3.4   Emissions

Tail gas from a Claus sulphur-recovery unit contains a variety of pollutants from direct process oxidation reactions including SO_2 and unreacted H_2S, other furnace side reaction products such as reduced sulphur compounds and mercaptans (e.g., COS, CS_2) as well as small quantities of CO and VOC. These components may be emitted directly in older or very small uncontrolled Claus plants. The quantity and composition of sulphur components in the Claus plant tail gas are directly related to the sulphur recovery efficiency which will depend on factors such as: the number of catalytic stages, the concentration of H_2S and other contaminants in the feed gas, the stoichiometric balance of inlet gaseous components, operating temperatures, combustion efficiencies and catalyst maintenance. Typical Claus plant efficiencies range from 94-96% for two-stage units to 97-98.5% for four-bed catalytic plants and, because the process is thermodynamically limited, the tail gas still contains percent quantities of sulphur compounds which may be further treated for recovery and emission control. When feed gas flow is much lower than the dimensional flow for the Claus unit and when sour gas composition and flow is fluctuating between 80 and 90 % it can be difficult to achieve these high efficiencies. Efficiencies between 80 and 90 % have been reported for such difficult conditions.

3.5   Controls

Tail gas emission reduction from the Claus process is normally achieved by one of the three following types of control methods:

Claus Reaction Extension to Lower Temperature Liquid Phase Several processes are available which extend the Claus reaction into a lower temperature liquid phase, whereby enhanced conversion occurs at cooler temperatures in the catalytic stages. These processes

result in overall higher sulphur recoveries (e.g. 98-99%) and correspondingly reduced sulphur compound emissions in the tail gas.

Tail Gas Scrubbing Although several types of tail gas scrubber variations exist, two generic types are used to reduce sulphur emissions from the sulphur recovery process - oxidation or reduction tail gas scrubbers. For example, the Wellman-Lord oxidation scrubber system is used in combination with tail gas incineration, whereby the Claus plant sulphur compounds are oxidized to SO_2 during combustion and this component is absorbed by sodium sulphite/bisulphite solution with associated release of the off gas. The bisulphite solution is then decomposed by boiling to produce a sodium sulphite precipitate for re-use and a regenerated SO_2 stream which is recycled back to the Claus process. Up to 99.9% sulphur recovery can be accomplished with the system. In reduction scrubbers, tail gas sulphur compounds are converted by hydrogenation to H_2S which is either removed by conventional amine scrubbers for regeneration/recycle back to the Claus process or converted to sulphur outside the Claus unit using the Stretford lean H_2S-to-sulphur process.

Tail Gas Incineration Claus plant emissions may also be directly incinerated to convert the more hazardous reduced sulphur compounds to SO_2 under proper combustion conditions for release to the stack.

4   SIMPLER METHODOLOGY

The simpler methodology would be to inventory using area source methods and assume that all sulphur recovery operations are two-staged and have no control technology for tail gas cleanup. Emissions of SO_2 would then be conservatively estimated by using the highest uncontrolled emission factor and the total amount of sulphur produced through sulphur recovery processes. This would provide an upper bound to the likely emissions, but in the absence of more detailed production information represents an acceptable estimation method to use.

5   DETAILED METHODOLOGY

The preferred methodology would involve either a sulphur mass balance or the measurement of emissions from each plant to develop site-specific emission factors or emissions data for all potentially significant sources.

In the mass balance approach, at minimum, the sulphur content and volumes of sulphur recovery plant feed gas materials (e.g., sour gas streams or absorption tower sulphide off-gas) are needed to define the mass of input sulphur. This may also comprise sulphur input from sour water stripping of waste-waters. In conjunction with the mass of elemental sulphur produced, the quantity of sulphur in tail gas emissions requires determination. This may be done by calculating the sulphur recovery efficiency with a knowledge of the number and type of sulphur recovery units including Claus plant catalytic stages and/or measuring the volume and sulphur content of the tail gas. Account should also be made of SO_2 emissions associated with catalyst regeneration, where practised on-site, as well as unaccounted losses to confirm

the balance. Upon conversion to SO_2, the emissions from sulphur recovery operations (expressed as kg SO_2 per Mg pure elemental sulphur produced) may be calculated by:

$$SO_2 \ emissions \ (kg \ / \ Mg) \ = \ \frac{100 \ - \ \%recovery}{\%recovery} \ x \ 2000$$

In instances where the tail gas is treated further by scrubbers or incinerators, the emissions may be best determined by stack testing. Emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At this time, new site-specific emission factors should be derived based on testing or mass balance determinations.

Accordingly, the most reliable emission estimation alternative is to inventory each sulphur recovery installation as a point source, using site-specific process and production information. This would ideally include site-specific information on the average percent sulphur recovery, which can be used to derive site-specific emission factors by assuming that all sulphur is released as SO_2. If the sulphur recovery information is not available, the appropriate emission factors from section 8 should be used.

6   RELEVANT ACTIVITY STATISTICS

Emission factors are based on the production of elemental sulphur.

7   POINT SOURCE CRITERIA

The average production rate of a sulphur recovery plant in the U.S. varies from 50 to 200 Mg per day. Using a typical production rate per day of 124 Mg, an uncontrolled emission rate of over 4000 Mg SO_2 per year would be expected, while a similar facility with the highest level of control would emit just under 1000 Mg (see section 8 for emission factors). It is therefore recommended that all sulphur recovery facilities be inventoried as point sources.

8   EMISSION FACTORS, QUALITY CODES AND REFERENCES

U.S. EPA emission factors for modified Claus sulphur recovery plants are summarised in Table 2.

The CONCAWE Air Quality Management Group (Concawe, 2006) has identified a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR),

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found

at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.

The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

For Sulphur Recovery Plants CONCAWE suggests the U.S. EPA methodology.

Table 2: Modified Claus Sulphur Recovery Plant Emission Factors (U.S. EPA 1994)

Number of Catalytic Stages	Average Percent Sulphur Recovery[a]	SO_2 (kg/Mg Sulphur Produced)	Emission Factor Rating
Two, uncontrolled	93.5[c]	139[b,c]	E
Three, uncontrolled	95.5[d]	94[b,d]	E
Four, uncontrolled	96.5[e]	73[b,e]	E
Two, controlled[f]	98.6	29	B
Three, controlled[g]	96.8	65	B

[a] Efficiencies are for feed-gas streams with high H_2S concentrations. Gases with lower H_2S concentrations would have lower efficiencies. For example, a 2- or 3-stage plant could have a recovery efficiency of 95% for a 90% H_2S stream, 93% for 50% H_2S and 90% for 15 H_2S.
[b] Based on net weight of pure sulphur produced. The emission factors were determined using the average of the percentage recovery of sulphur.
[c] Typical sulphur recovery ranges from 92 to 95 percent.
[d] Typical sulphur recovery ranges from 95 to 96 percent.
[e] Typical sulphur recovery ranges from 96 to 97 percent.
[f] Test data indicated sulphur recovery ranges from 98.3 to 98.8 percent.
[g] Test data indicated sulphur recovery ranges from 95 to 99.8 percent.

9   SPECIES PROFILES

Species profiles are not required for this sector.

10   UNCERTAINTY ESTIMATES

Emission factors for this sector are based on sulphur recovery ranges for typical operations. These indicate that, for a given process, total recovery rate variations range from as little as 0.5% to as much as 5%. Therefore, given accurate process and production information, estimates of SO_2 emissions from these facilities should be accurate to within 10 percent.

11   WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The simpler methodology relies on emission factors that may not be representative of the process.

12   SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

All sulphur recovery plants should be inventoried as point sources. However, if the simpler methodology is used, emissions can be disaggregated based on plant production capacities.

13   TEMPORAL DISAGGREGATION CRITERIA

Sulphur balances are often conducted for petroleum refineries on a daily basis. Such plant-specific information may be used to temporally resolve emissions.

14   ADDITIONAL COMMENTS

SNAP Coding for sulphur recovery plants is somewhat awkward in that it is coded under petroleum refineries but is not exclusively found at these locations.

15   SUPPLEMENTARY DOCUMENTS

16   VERIFICATION PROCEDURES

17   REFERENCES

Air and Waste Management Association, 1992. "Air Pollution Engineering Manual." Edited by A.J. Buonicore and W.T. Davis, Van Nostrand Reinhold, New York.

Canadian Petroleum Products Institute and Environment Canada, 1991. "Atmospheric Emissions from Canadian Petroleum Refineries and the Associated Gasoline Distribution System for 1988." CPPI Report No. 91-7 prepared by BH Levelton and Assoc. and RTM Engineering Ltd.

Concawe, 2006. Air pollutant emission estimation methods for EPER and PRTR reporting by refineries (revised), Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Emission Reporting Methodologies (STF-64), P. Goodsell (Technical Coordinator), Report no. 9/05R, Brussels April 2006

Environment Canada, 1987. "Environmental Status Report for the Canadian Petroleum Refining Industry 1983-1984." Conservation and Protection Report EPS 1/PN/1.

U.S. Environmental Protection Agency (U.S.EPA), 1993. " 5.18 Sulfur Recovery." in Supplement F to Compilation of Air Pollutant Emission Factors - Volume I: Stationary Point and Area Sources. AP-42. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

18   BIBLIOGRAPHY

19   RELEASE VERSION, DATE AND SOURCE

Version :   1.3

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Source :   Marc Deslauriers
                      Environment Canada
                      Canada

Integrated with CONCAWE (CONCAWE, 2006) suggestion by:
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