Advanced Technologies for Desulphurisation of Coke Oven Gas

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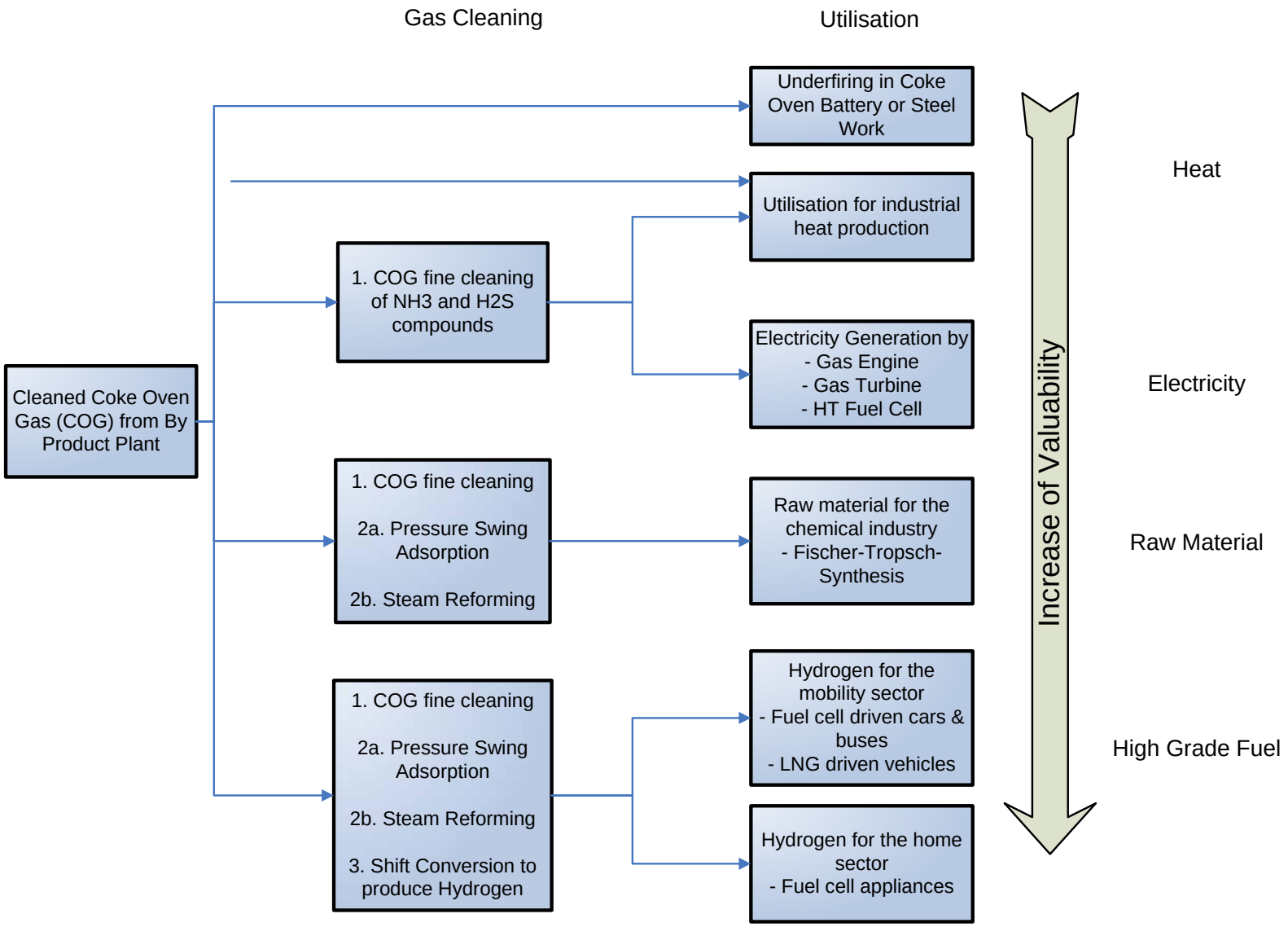
Alternative Ways of Using COG



Purity Requirements for COG

Utilisation	NH_3 (mg/Nm^3 COG)	H_2S (mg/Nm^3 COG)	HCN (mg/Nm^3 COG)
Coke Oven Underfiring	< 10 – 200	< 300 – 900	< 500 – 1000
Industrial Boilers	< 10 – 200	< 300 – 500	< 500 – 1000
Gas Motor	< 15	< 300 – 500	unspecified
Low efficient Gas Turbine	unspecified	< 500	unspecified
High efficient Gas Turbine (e.g. for Combined Cycle)	< 0,3	< 1,2	< 7,0
HT Fuel Cell	< 0,5	< 2,0	< 150
Fischer Tropsch Synthesis	< 1 ppmV	$H_2S + COS + CS_2$ < 1 ppmV	< 1 ppmV

Survey of desulphurisation processes

Wet Oxidation Route

Stretford

H_2S is scrubbed from the coke oven gas by a sodium carbonate solution (Na_2CO_3) and elemental sulphur (S°) is yielded using vanadate (VO_3) as an intermediate. Regeneration of the scrubbing liquid takes place by aeration (O_2), using anthraquinone disulphonic acid (ADA) as an intermediate.

Takahax
Thylox
Perox
Fumaks-Rhodacs

Absorption / Stripping Route

ASK or Diamex

H_2S is scrubbed from the coke oven gas by a NH_3 solution. The NH_3 solution is derived from the NH_3 scrubber. The H_2S and NH_3 are stripped from the washing liquor by steam stripping and the vapours are led to a Claus plant or a sulphuric acid plant.

Vaccuum Carbonate
Sulfiban
DESULF

General Comparison of both Process Routes

Wet Oxidation Route

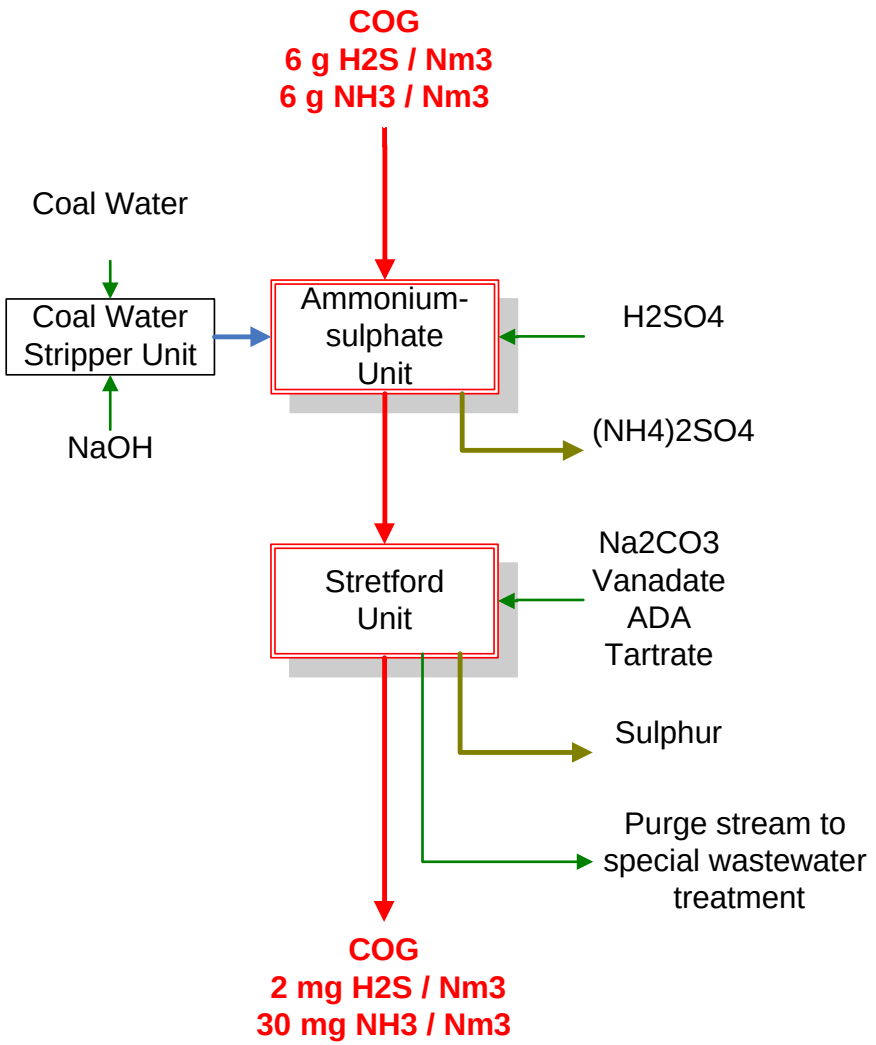
- Better desulphurisation efficiency of ca. 99.9% achieving residual H_2S concentrations as low as 1 mg/Nm^3 in the COG.
- Removal of most of the hydrogen cyanide from the COG forming sodium thiocyanide which are purged by a liquid stream to prevent salting out of the chemicals.
- Wastewater usually to be treated separately owing to the presence of compounds showing detrimental effects on the BET.
- Applicable at new and existing plants.
- Applicable also for low desulphurisation capacities starting from 400 Nm^3/h COG.

Absorption / Stripping Route

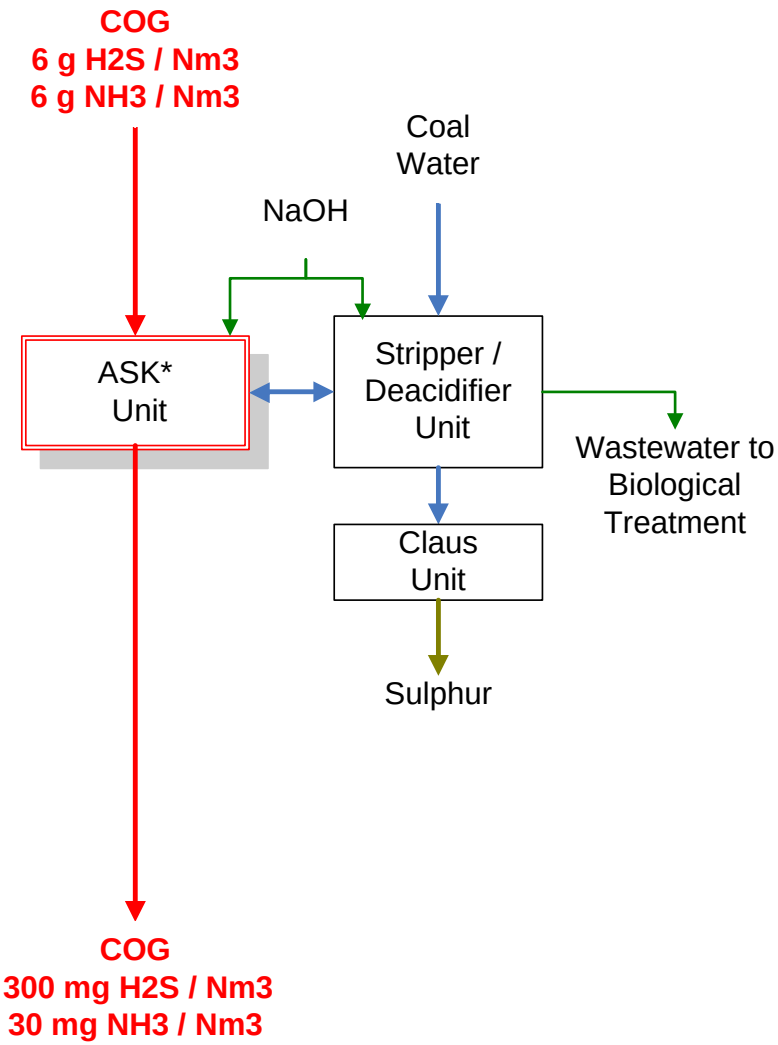
- Absorptive processes usually do not exceed 95% desulphurisation efficiency achieving residual H_2S concentrations in the COG of ca. 300 mg/Nm^3.
- The discharge of small wastewater flows to the BET does not require any further treatment.
- Applicable at new and existing plants.

Plant Configuration for TCO

Wet Oxidation Process



Absorption / Stripping Process



Assumptions / Parameters of the TCO elaboration

(on European basis) – 1/3

Parameter	Unit	Ammonia Sulphate / Stretford	ASK / Stripper Unit / Claus Plant
COG production	Nm^3/h	42,000	42,000
Crude COG			
H_2S	g/Nm^3	6	6
NH_3	g/Nm^3	6	6
Clean COG			
H_2S	mg/Nm^3	2	300
NH_3	mg/Nm^3	30	30

Assumptions / Parameters of the TCO elaboration

(on European basis) – 2/3

Price of Consumables	Parameter	Unit	Ammonia Sulphate / Stretford Unit	ASK / Stripper / Claus Unit
	Consumables			
11.90 €/t	Steam	t/d	154	264
0.34 €/kWh	Electricity	kWh/d	11,900	6,600
128.00 €/t	H_2SO_4 (98%)	t/d	17.5	---
7.70 €/kg	ADA	kg/d	24	---
27.00 €/kg	Vanadate	kg/d	10	---
5.50 €/kg	Tartrate	kg/d	13	---
370.00 €/t	Soda	t/d	2.6	---
110.00 €/t	Caustic Soda	t/d	9.6	9.6

Assumptions / Parameters of the TCO elaboration

(on European basis) – 3/3

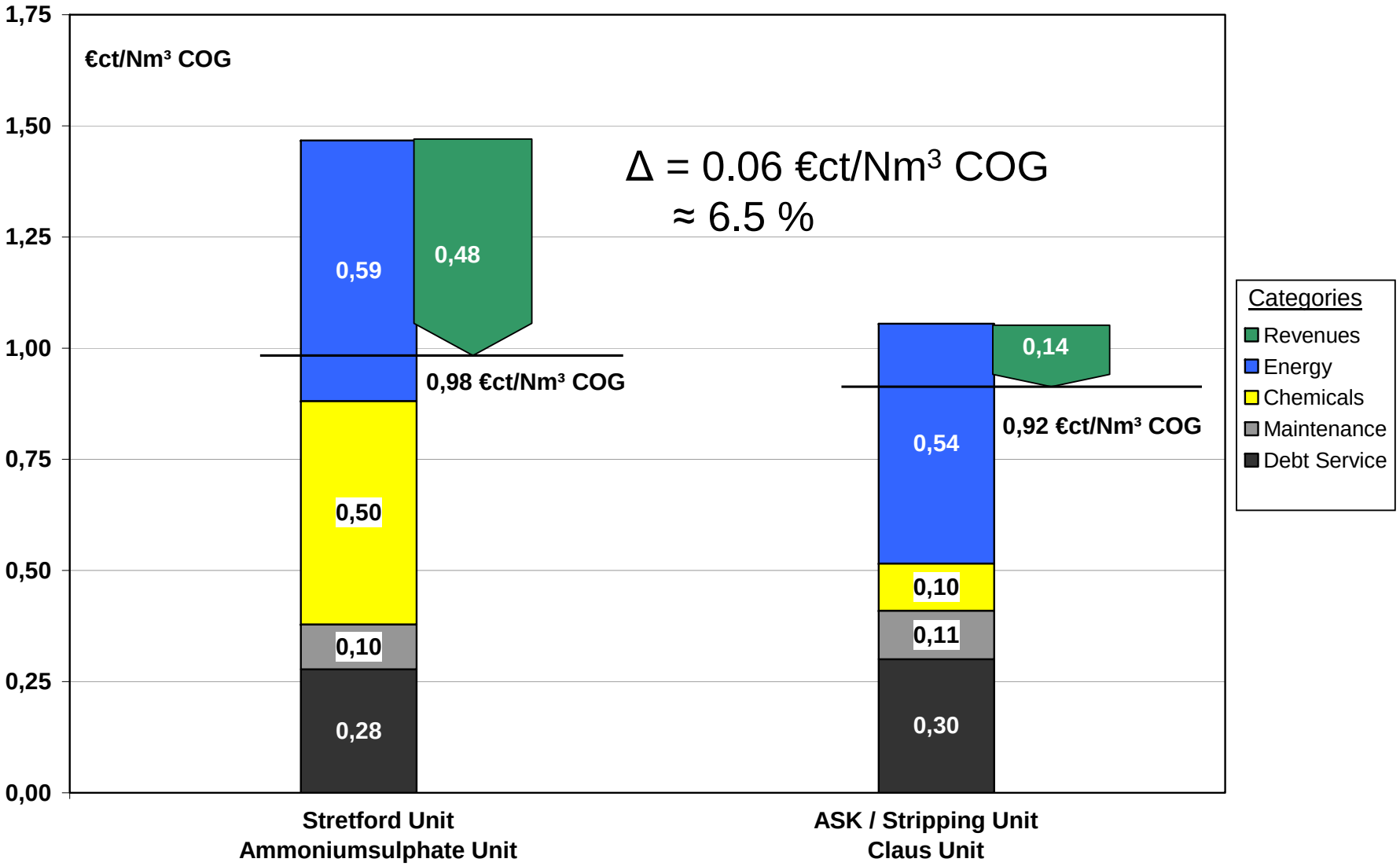
Parameter	Unit	Ammonia Sulphate / Stretford	ASK / Stripper Unit / Claus Plant
Products			
Sulphur	t/d	4.8	5.4
Ammonium Sulphate	t/d	23.5	--
Revenues			
Sulphur	€/t	125	250
Ammonium Sulphate	€/t	180	--
Annual Debt Service on Capital Costs	%	11	11
Annual Maintenance on Capital Costs	%	4	4

Sulphur Quality

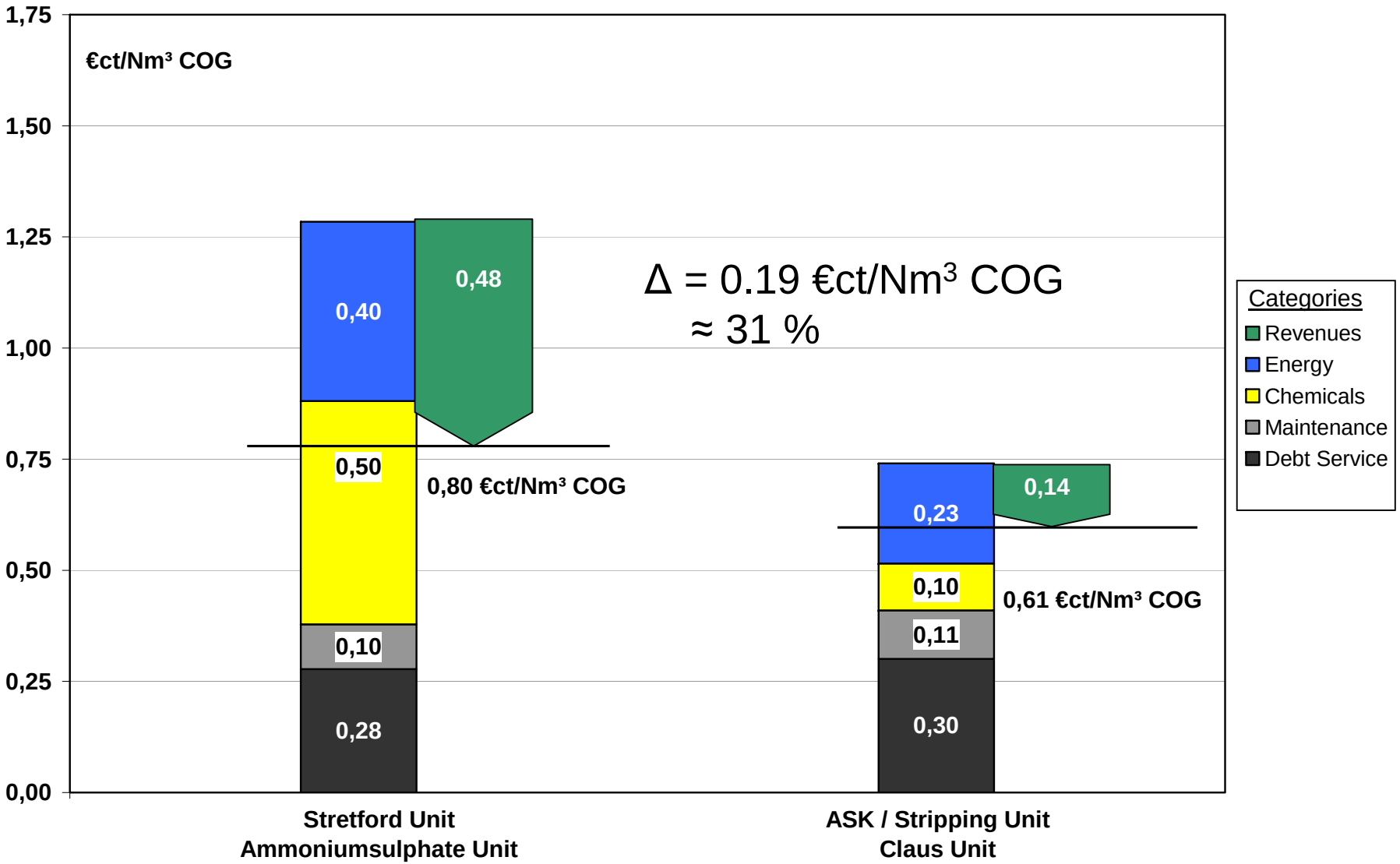
Stretford Sulphur
(Solidified Product after Autoclave)

Claus Sulphur
(Solidified Sample after S-Separator)

TCO comparison (incl. costs for steam)



TCO comparison (without costs for steam)



Sale Scenario Impact on TCO

Sale Scenario			Process Route	Cleaning Costs € ct / Nm^3 COG			
Scenario	$(NH_4)_2SO_4$ €/t	S° €/t		Scenario (Steam at costs)	Δ	Scenario (Steam at no costs)	Δ
Medium level	180	125	Stretford	0.98	+7%	0.80	+31%
	---	250	ASK	0.92		0.61	
High level	180	---	Stretford	1.04	+18%	0.86	+51%
	---	320	ASK	0.88		0.57	
Low level	120	---	Stretford	1.19	+29%	1.00	+64%
	---	250	ASK	0.92		0.61	

Conclusions

Wet Oxidation Route

Advantages:

- High cleaning efficiency (<2 mg H_2S / Nm^3 COG, 30 mg NH_3 / Nm^3 COG)
- No HP-scrubbing required

Disadvantages:

- Higher operating costs
- NH_3 and HCN pre-scrubbing required
- Catalyst as consumable required
- Quality of Sulphur S° often deteriorated yielding lower revenues
- Contaminated wastewater streams need special treatment
- Susceptible for contamination
- Dependence on suppliers for catalyst and ADA (consumables)

Absorption / Stripping Route

Advantages:

- Lower operating costs
- No consumable catalyst required
- NH_3-scrubbing included
- High quality Sulphur S° with high revenues
- No contaminated wastewater; wastewater directly delivered to the BET

Disadvantages:

- Lower cleaning efficiency (300 mg H_2S / Nm^3 COG, 30 mg NH_3 / Nm^3 COG)
- HP-scrubbing necessary to achieve a H_2S concentration of below 2 mg/Nm^3 in the clean gas (if demanded)

Thank you for your attention !