DRAFT SOLUTIONS –PART B

Part B. 1. Chlorine production and Purification

Note : Answers can be derived in the main by referring to the text, Section 4.12

(a) See Section 4.12.1 in Chapter 4
(b) Essential feature is the membrane which allows passage of sodium ions but not hydroxide or chloride ions.
   Key advantage of the membrane cell is the elimination of mercury from the process system. One disadvantage of the membrane cell is that the caustic soda concentration of the product from the cell is limited to around 35% compared with around 50% for the mercury cell. This requires increased steam consumption in an evaporation step. A further potential consideration is that the membrane will need cleaning and eventual replacement with some secondary impacts.
(c) (i) Sulphuric acid consumption can be minimized by use of chilled water in the cooling step prior to drying. Further opportunity exists in refrigerating the acid used in the drying step.
   (ii) Dilute sulphuric acid leaving the drying plant could be treated to remove dissolved chlorine (eg by stripping the chlorine out with air) followed by concentration in an evaporator. A difficulty in evaporation is the steep boiling point vs concentration curve for sulphuric acid. Note: This problem is examined in greater detail in Part D, Problem 2.
(d) (i) and (ii) Use equations 7.1 and 7.2. Approximate power is 110 kW for adiabatic compression, requiring an electric motor drive of 165kW allowing for compressor, transmission and drive efficiencies. Approximate discharge temperature leaving compressor is 140°C. [Note: Numbers have been scaled from a similar set of conditions]
   (iii) Air cooling would reduce the probability of water ingress through heat exchanger leakage, thus increasing the moisture content and corrosiveness of the chlorine gas.

Part B. Question 2. PVC production from vinyl chloride monomer.

Note : Answers can be derived in the main by referring to the text, Section 4.16

(a) Polymerisation reaction is exothermic. Cooling is generally achieved by cooling water circulating in the external jacket of the reactor. Other means are possible. eg a supplementary vapour condenser.
(b) Reaction kinetics slow as conversion progresses. Reaction rate is judged to be economically non-viable when conversion is around 90% of the monomer.
(c) Refrigeration is necessary to condense the VCM from the vent gases, to maximize VCM revovery and minimize VCM emissions.
(d) VCM is flammable and a carcinogen. Its release to atmosphere in unacceptable from a toxicological viewpoint. Hence the vent stream, which still contains a residue of VCM, is incinerated.
(e) Possible causes of 'out of specification' PVC are:
   • Use of a reaction stopper in the reactor (should a runaway reaction occur)
   • Fouling of surfaces within the reactor
   • Fouling of product during the drying stage

Question 3. Waste Minimisation in Nitric Acid Production

Nitric acid production, encompassing the steps of ammonia oxidation, gas cooling, and gas absorption has been established for over a century. The main reactions in the process include:

Ammonia oxidation: $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$ +905 kJ

Oxidation of nitric oxide: $2NO + O_2 \rightarrow NO_2$ +113 kJ

Absorption of nitrogen dioxide in water: $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$ +116 kJ* (* for 60%w/w acid)
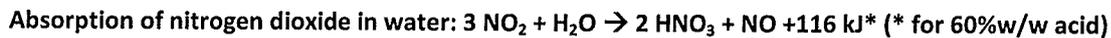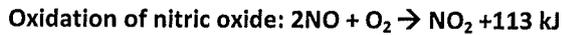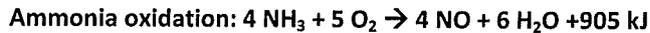
While the process has been in commercial use for a long time, and appears simple, the chemistry is complex. Reference to both academic (for example Moulin et al 2001, detailed on Brennan p185) and process licensing literature (for example ThyssenKrupp Uhde publication 'Nitric Acid' (http://www.thyssenkrupp-uhde.de/en/company.html) is recommended. Moulin et al 2001 provide some details regarding the complexity of the chemistry in the reaction, cooling and absorption steps. The complex chemistry of reactions in the absorption tower is also discussed by Twigg (see reference list for Chapter 4).

(a) (i) Process wastes

Nitrous oxide (N_2O) and nitric oxide (NO) are formed in the reaction step, and both gases are present in the tail gas leaving the nitric acid absorption tower providing the main effluent containing process waste. The ThyssenKrupp Uhde publication reports 1 to 2% of the ammonia fed to the reactor being converted to N_2O. While most of the NO formed in the reactor is oxidized to NO_2 prior to absorption, some residual NO remains which has limited solubility in the nitric acid. Tail gas may also contain traces of unabsorbed NO_2 and, depending on design of the absorption column, entrainment of HNO_3.

Spillages, leakages and fugitive emissions, arising for example from ammonia storage and handling, are also potential sources of waste from process materials.

N_2O contributes to global warming potential, while NO (and NOx) contribute to acidification and nutrification potentials, and to human toxicity. NH_3 contributes to nutrification potential and toxicity.

(b) Utility wastes

Utility wastes are derived from generation of
- electricity for driving air compressor, ammonia feed pump, and circulating nitric acid pump in absorber
- cooling water used in condenser prior to absorber and in absorption column
- electricity and cooling water consumed in refrigeration, if employed, for example in ammonia storage or nitric acid absorption.

The wastes derived from cooling water and electricity use depend on the quality of water and fuel used in generating the utilities, as well as the cycles used in utility generation. See Chapter 6 for basic information on utilities generation and use, and Chapter 11 (sections 11.2 and 11.3 dealing with life cycle inventories).

Heat recovery opportunity is provided through cooling the gas stream leaving the reactor at around 900°C enabling high pressure steam generation; this steam can be used in a steam turbine for driving the main air compressor. Energy recovery is also possible through use of a tail gas turbine located on the outlet of the absorption tower. These energy recovery steps allow some credits to be claimed for avoided consumptions and emissions from fuel combustion.

(c) Ullmann lists four basic approaches to reduce tail gas NOx emissions
- improved absorption in the gas absorption column (see part (d))
- chemical scrubbing (a range of scrubbing liquors have been used and investigated including ammonia and hydrogen peroxide)
- adsorption, which has had relatively little industrial application
- catalytic reduction processes, classified as selective and nonselective

The ThyssenKrupp Uhde publication reports a catalytic abatement process (EnviNOx[®]) which reduces both the N_2O and NOx components in the tail gas. N_2O is first converted catalytically to nitrogen and oxygen

$$N_2O \rightarrow N_2 + 0.5\ O_2 + 82\ kJ$$
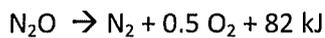
This is followed by a second catalytic reduction of NOx with ammonia to form N_2 and water

$$4\ NO + 4NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O + 1628\ kJ$$

$$3\ NO_2 + 4\ NH_3 \rightarrow 3.5N_2 + 6\ H_2O + 1387\ kJ$$

The following simplified table summarises environmental burden and cost considerations for some alternative treatment approaches.

Treatment method	Environmental burden	Cost consideration
Improved absorption in gas absorption column	Increased energy consumed through higher pressure, lower temperatures	Increased capital and operating costs of absorber
Chemical scrubbing of tail gas	Energy consumed; any effluents derived from solvent purging	Increased capital and operating costs
Adsorption	Adsorbent regeneration or disposal	High capital costs
Catalytic reduction	Energy consumed in tail gas preheating, pressure losses (partially recovered in turbine)	Costs of upstream heater, reactor, initial and replacement catalyst

(d) Changes in process conditions in the absorber include

(i) Increased pressure

(ii) Lower temperature, using lower temperature coolants

These approaches, including the use of refrigeration, are discussed by Ullmann. The use of pressure has been used commercially with so-called medium pressure (4-6 bar abs), high pressure (10-12 bar abs), and dual pressure processes (see ThyssenKrupp Uhde). See additional reference ThyssenKrupp Uhde publication 'Nitric Acid' (http://www.thyssenkrupp-uhde.de/en/company.html

(e) Potential for steam generation.

At 20 bar, temperature of saturated steam = 212°C

This condition could be achieved in a waste heat boiler with a temperature driving force of 22° C at the gas outlet end of the boiler. The steam could then be superheated from 212° C to 330°C in a separate superheater, using heat recovered at a higher temperature of gas leaving the reactor. A constraint would be ensuring that cooling of the gases leaving the reactor occurred quickly enough to minimise undesirable side reactions.

Potential for steam use.

Superheated steam could be used within the nitric acid plant by expansion through a turbine to drive the main air compressor. Exhaust steam at a low pressure (even below 1 bar abs) could be used for process heating such as vaporizing ammonia feed for supply to the reactor.

Overall steam quantities would need to be confirmed by energy balances. Expansion through the turbine would approach an isentropic expansion. Use for process heating would approach isothermal condensation.

Part B Question 4.

(a) (i) Theoretical flame temperature is calculated assuming
- Adiabatic combustion
- Heat of combustion is exchanged with sensible heat of flue gas

(ii) Excess air is used to ensure complete combustion. The extent of excess air depends on the fuel and the burner design used

(iii) Major source of inefficiency is heat loss in the flue gas leaving the furnace exhaust stack
(iv) Two common losses are
- Boiler blowdown, necessary to limit dissolved solids concentration of boiler water
- Steam use in dearator to increase temperature and hence reduce solubility of oxygen

(b) CH_4 + $2O_2$ → CO_2 + $2H_2O$
   16   64   44   36
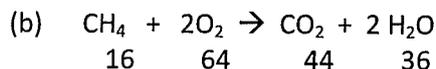
Enthalpy of saturated steam at 10 bar, 180°C = 2778 kJ/kg
Assume steam condensate returns with make-up water at 100°C
Enthalpy = 417 kJ/kg
Heat required per kg steam = 2361 kJ/kg
Boiler duty = $\dfrac{12 \times 1000 \times 2361}{3600}$ = 7870 kW
Furnace duty = $\dfrac{7870}{0.75}$ = 10,493 kW

(i)   Fuel burned = $\dfrac{10493}{50 \times 1000}$ = 0.21 kg/s

(ii) CO_2 formed = $\dfrac{0.21 \times 44}{16}$ = 0.578 kg/s

   H_2O formed   = $\dfrac{36 \times 0.21}{16}$ = 0.473 kg/s

   O_2 consumed = $\dfrac{64 \times 0.21}{16}$ = 0.840 kg/s

If 10% excess air is used,

   O_2 in flue gas = 0.1 x 0.840 = 0.084 kg/s

N_2 in flue gas = $\dfrac{76.7 \times 0.840 \times 1.1}{23.3}$ = 3.042 kg/s

Flue gas composition

	Mass flow rate (kg/s)	Composition (% w/w)
CO_2	0.578	13.8
H_2O	0.473	11.3
N_2	3.042	72.8
O_2	0.084	2.01
Total	**4.177**	**100**

(c) (i) $2H_2 + O_2 = 2H_2O$

   4   32   36
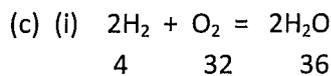
H_2 fuel burned = 200/3600 = 0.056 kg/s

Heat provided = 0.056 x 142 x 1000 =   7889 kW

Total heat required   =   10493 kW

Residual heat required from natural gas =   2604 kW

Required natural gas consumption = $\dfrac{2604}{50 \times 1000}$ = 0.052 kg/s

Reduction in natural gas consumption = 0.158 kg/s

(ii) Resulting reduction in CO2 emissions = 0.158 x 44 /16 = 0.435 kg/s

   Note that some thermal NOx will be produced resulting from the hydrogen combustion

(d) Expansion of the condensate through the valve will be isenthalpic.

Let Z be the fractional proportion of the steam which flashes off. Then making a heat balance over the expansion

763 = Z x 2675 + (1-Z) x 417 .

Z =0.153.

(e) In this case, the expansion through the turbine is assumed to be isentropic.

Making an entropy balance

Entropy of the incoming steam = 7.124 kJ/kg

Entropy of the exit steam = 7.124 kJ/kg

Entropy of saturated steam at 1 bar = 7.359 kJ/kg, slightly above the entropy of the exit steam.

This indicates the exit steam will have a temperature of approximately 100C and be slightly wet.

Let Z be the fraction of condensate in the exit steam. Then $7.124 = 7.359 (1-Z) + Z(1.303)$ and $Z = 0.039$.

(f) Oxygen removal occurs in two steps:
- Deaeration sparging of water with steam at atmospheric pressure → decreases oxygen solubility
- Treatment of remaining oxygen by sodium sulphite or hydrazine addition
  $Na_2SO_3 + 0.5O_2 \rightarrow Na_2SO_4$
  $N_2H_4 + O_2 \rightarrow 2H_2O + N_2$

Part B Problem 5

(a)
Heat load on cooling tower
$0.52 * 1000 * 4.2 * 22 = 48048$ kW
m3/s * kg/m3 * kJ/kg K
If latent heat of evaporation of water = 2400 kJ/kg
Evaporation = 48048/2400 = 20kg/s (or ~3.8% water citculation rate)

(b)
Neglecting entrainment losses
M = E + P
30 * M = 300 * P
Solving P = 2.2 kg/s
M = 22.2 kg/s

(c)
Alkalinity, hardness, sulphates, chlorides(corrosion) - see pp101,121,122

(d)
Power = Q* h * d / e where Q = volumetric flowrate, h = developed head,
d = density, e = combined efficiency of pump and electric motor

Power = 0.52*600000/0.60*1000 = 520 kW

(e)
Reliability of cooling water supply is a key consideration.
Hence provide redundancy for both pump and drive
Possible options :
(i) 2 pumps, 1 electric motor driven, 1 steam turbine driven
(ii)3 pumps, 2 operational (electric motor driven), 1 standby (steam turbine driven)

(f)
Maximum inlet temperature is governed by the maximum wet bulb temperature
of ambient air with allowance for temperature difference between air and water
For Melbourne, this would be approximately 28°C in summer conditions.
Maximum outlet temperature is governed by scaling considerations on heat
exchanger surfaces. Typical rule of thumb is within the range of 45 to 50°C.

Part B Problem 6

This is an open ended problem where the solution depends on the material selected, and the commercial, industrial and location constraints assumed.