LIFE IN THE BLACK

A PICTORIAL ROMP
THROUGH LIFE WITH
HEAT TRANSFER AND CARBON

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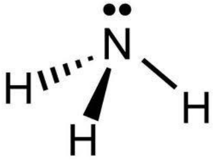
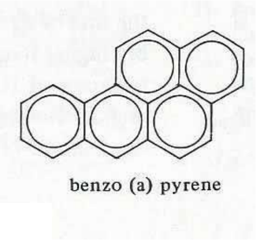
Faculty of Engineering and Design

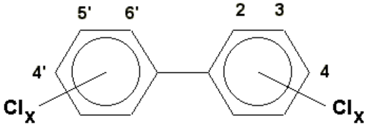
University of Bath, Bath, UK

Heat Transfer Society 22nd October 2013

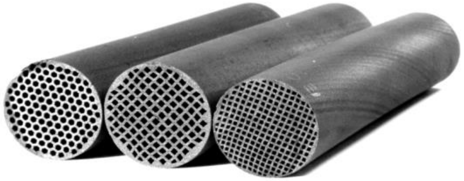
STRIKE THE ODD ONES OUT FROM MY LIFE IN THE BLACK

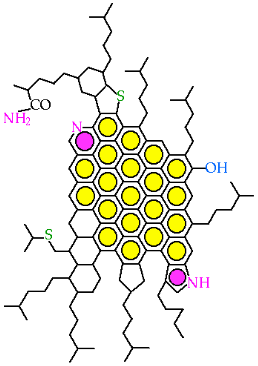


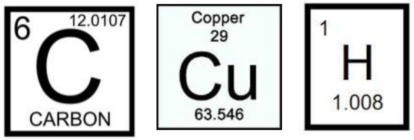

benzo (a) pyrene

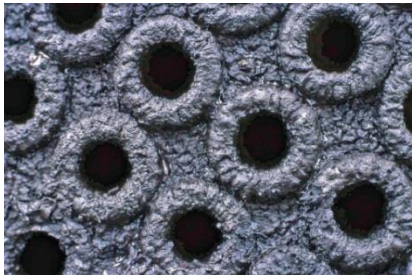


General formula for polychlorinated biphenyls

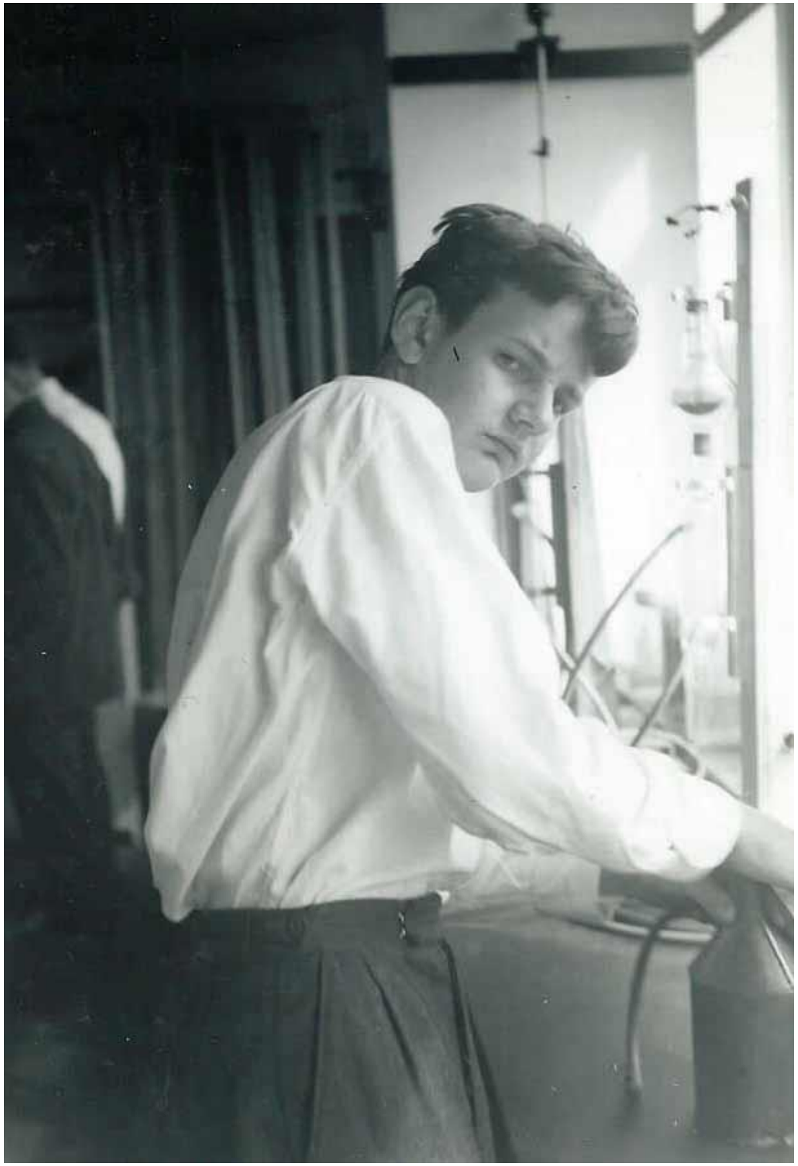


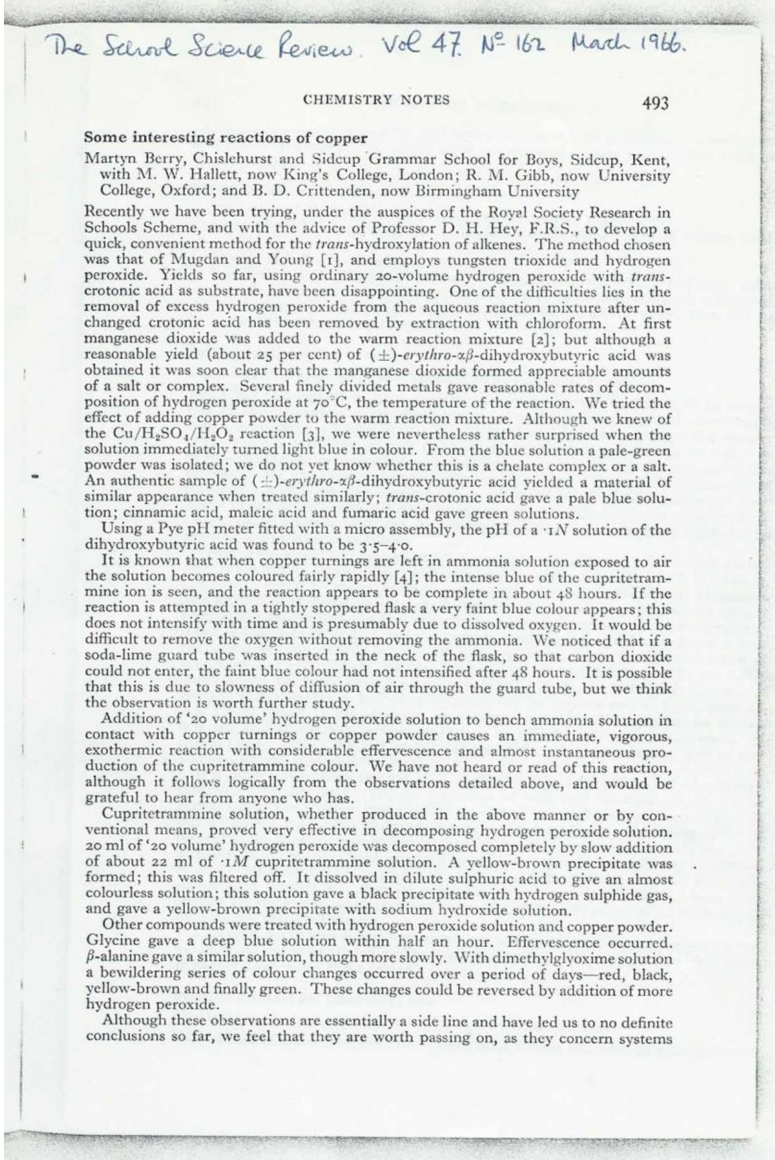






SOME INTERESTING REACTIONS OF COPPER





The School Science Review. Vol 47. № 162 March 1966.

CHEMISTRY NOTES 493

Some interesting reactions of copper

Martyn Berry, Chislehurst and Sidcup Grammar School for Boys, Sidcup, Kent, with M. W. Hallett, now King's College, London; R. M. Gibb, now University College, Oxford; and B. D. Crittenden, now Birmingham University

Recently we have been trying, under the auspices of the Royal Society Research in Schools Scheme, and with the advice of Professor D. H. Hey, F.R.S., to develop a quick, convenient method for the *trans*-hydroxylation of alkenes. The method chosen was that of Mugdan and Young [1], and employs tungsten trioxide and hydrogen peroxide. Yields so far, using ordinary 20-volume hydrogen peroxide with *trans*-crotonic acid as substrate, have been disappointing. One of the difficulties lies in the removal of excess hydrogen peroxide from the aqueous reaction mixture after unchanged crotonic acid has been removed by extraction with chloroform. At first manganese dioxide was added to the warm reaction mixture [2]; but although a reasonable yield (about 25 per cent) of (±)-*erythro*-αβ-dihydroxybutyric acid was obtained it was soon clear that the manganese dioxide formed appreciable amounts of a salt or complex. Several finely divided metals gave reasonable rates of decomposition of hydrogen peroxide at 70°C, the temperature of the reaction. We tried the effect of adding copper powder to the warm reaction mixture. Although we knew of the $Cu/H_2SO_4/H_2O_2$ reaction [3], we were nevertheless rather surprised when the solution immediately turned light blue in colour. From the blue solution a pale-green powder was isolated; we do not yet know whether this is a chelate complex or a salt. An authentic sample of (±)-*erythro*-αβ-dihydroxybutyric acid yielded a material of similar appearance when treated similarly; *trans*-crotonic acid gave a pale blue solution; cinnamic acid, maleic acid and fumaric acid gave green solutions.

Using a Pye pH meter fitted with a micro assembly, the pH of a ·1*N* solution of the dihydroxybutyric acid was found to be 3·5–4·0.

It is known that when copper turnings are left in ammonia solution exposed to air the solution becomes coloured fairly rapidly [4]; the intense blue of the cupritetrammine ion is seen, and the reaction appears to be complete in about 48 hours. If the reaction is attempted in a tightly stoppered flask a very faint blue colour appears; this does not intensify with time and is presumably due to dissolved oxygen. It would be difficult to remove the oxygen without removing the ammonia. We noticed that if a soda-lime guard tube was inserted in the neck of the flask, so that carbon dioxide could not enter, the faint blue colour had not intensified after 48 hours. It is possible that this is due to slowness of diffusion of air through the guard tube, but we think the observation is worth further study.

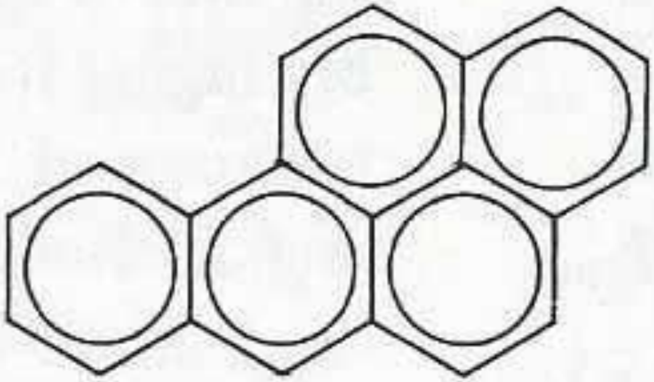
Addition of '20 volume' hydrogen peroxide solution to bench ammonia solution in contact with copper turnings or copper powder causes an immediate, vigorous, exothermic reaction with considerable effervescence and almost instantaneous production of the cupritetrammine colour. We have not heard or read of this reaction, although it follows logically from the observations detailed above, and would be grateful to hear from anyone who has.

Cupritetrammine solution, whether produced in the above manner or by conventional means, proved very effective in decomposing hydrogen peroxide solution. 20 ml of '20 volume' hydrogen peroxide was decomposed completely by slow addition of about 22 ml of ·1*M* cupritetrammine solution. A yellow-brown precipitate was formed; this was filtered off. It dissolved in dilute sulphuric acid to give an almost colourless solution; this solution gave a black precipitate with hydrogen sulphide gas, and gave a yellow-brown precipitate with sodium hydroxide solution.

Other compounds were treated with hydrogen peroxide solution and copper powder. Glycine gave a deep blue solution within half an hour. Effervescence occurred. β-alanine gave a similar solution, though more slowly. With dimethylglyoxime solution a bewildering series of colour changes occurred over a period of days—red, black, yellow-brown and finally green. These changes could be reversed by addition of more hydrogen peroxide.

Although these observations are essentially a side line and have led us to no definite conclusions so far, we feel that they are worth passing on, as they concern systems

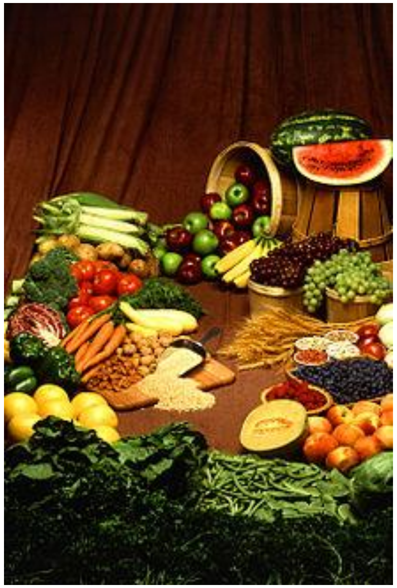
THE PROBLEM WITH POLYNUCLEAR AROMATIC HYDROCARBONS…



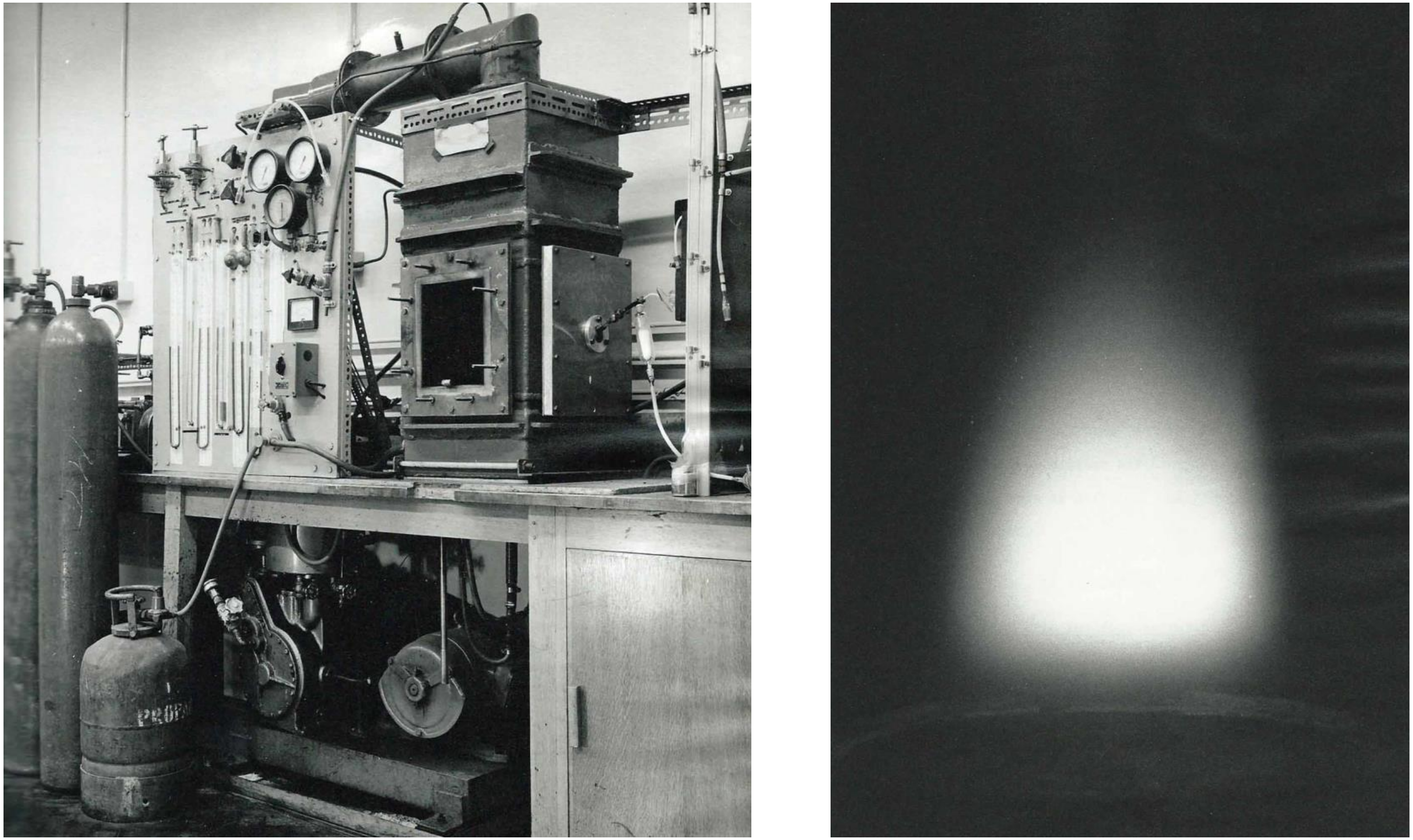
benzo (a) pyrene

95% carbon by weight

…IS THAT THEY ARE EVERYWHERE



THE SOOT MAKER



MEASUREMENT AND THE MECHANISM?

POLYCYCLIC AROMATICS IN PREMIXED FLAMES 363

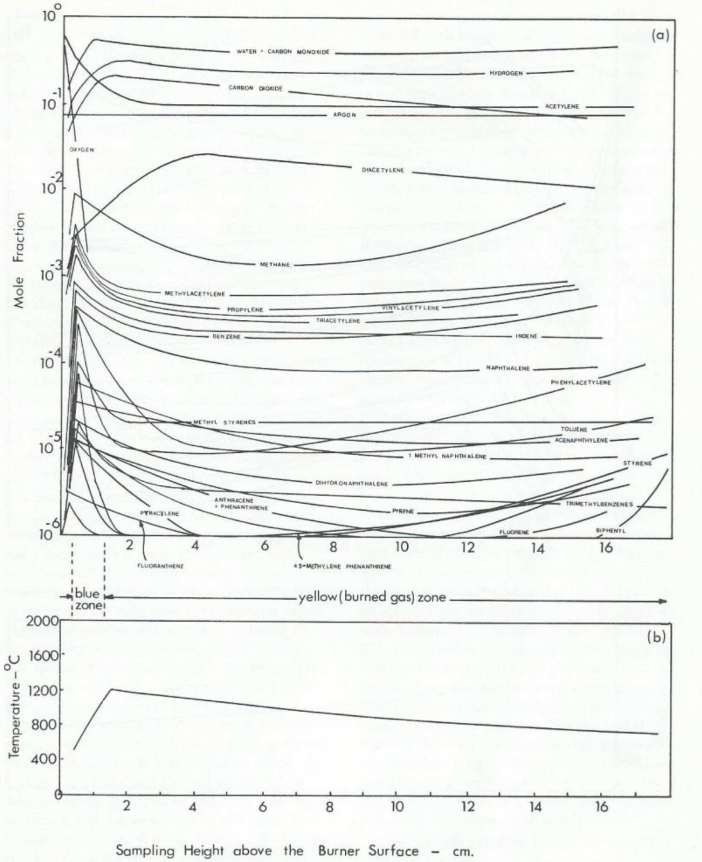


Fig. 1. Concentration and temperature profiles in Flame 1 (oxy-acetylene flame).

366 B. D. CRITTENDEN and RONALD LONG

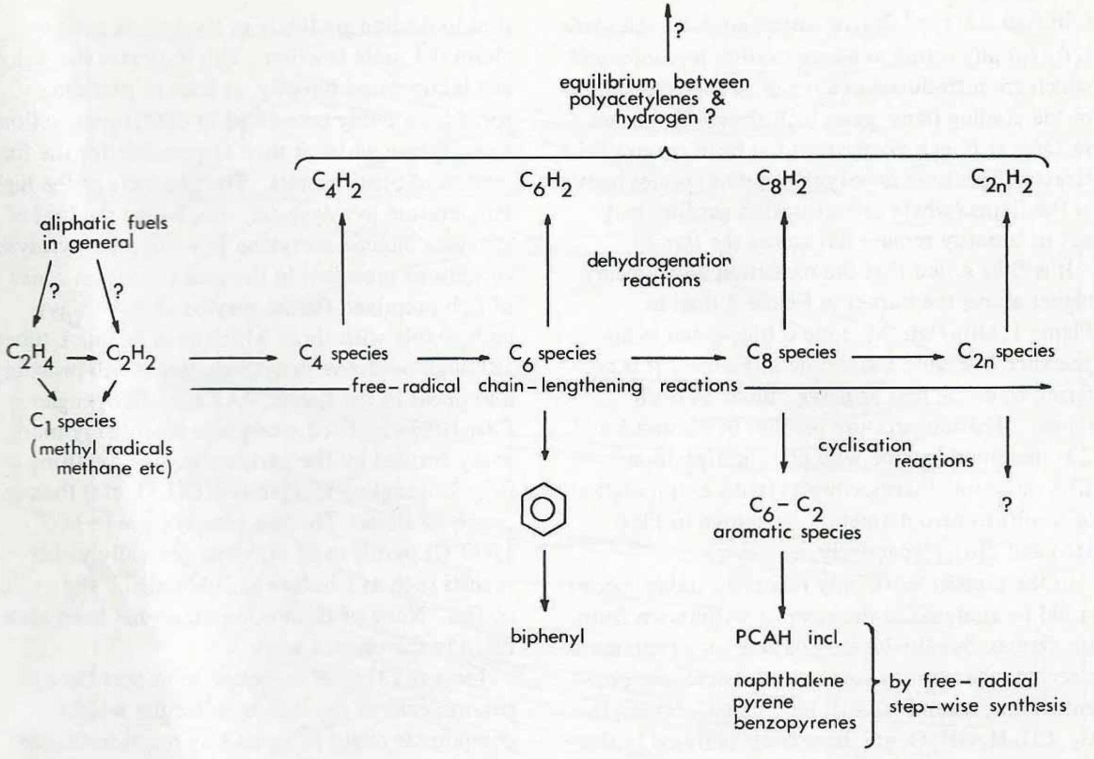
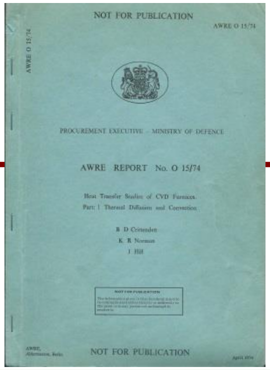


Fig. 3. Reaction scheme suggested to account for the formation of polyacetylenes and pcah in rich premixed flames.

THERMAL DIFFUSION AND NUCLEAR WARHEADS?



NOT FOR PUBLICATION

AWRE O 15/74

PROCUREMENT EXECUTIVE – MINISTRY OF DEFENCE

AWRE REPORT No. O 15/74

Heat Transfer Studies of CVD Furnaces.
Part 1 Thermal Diffusion and Convection

B D Crittenden
K R Norman
J Hill

AWRE,
Aldermaston, Berks

NOT FOR PUBLICATION

April 1974

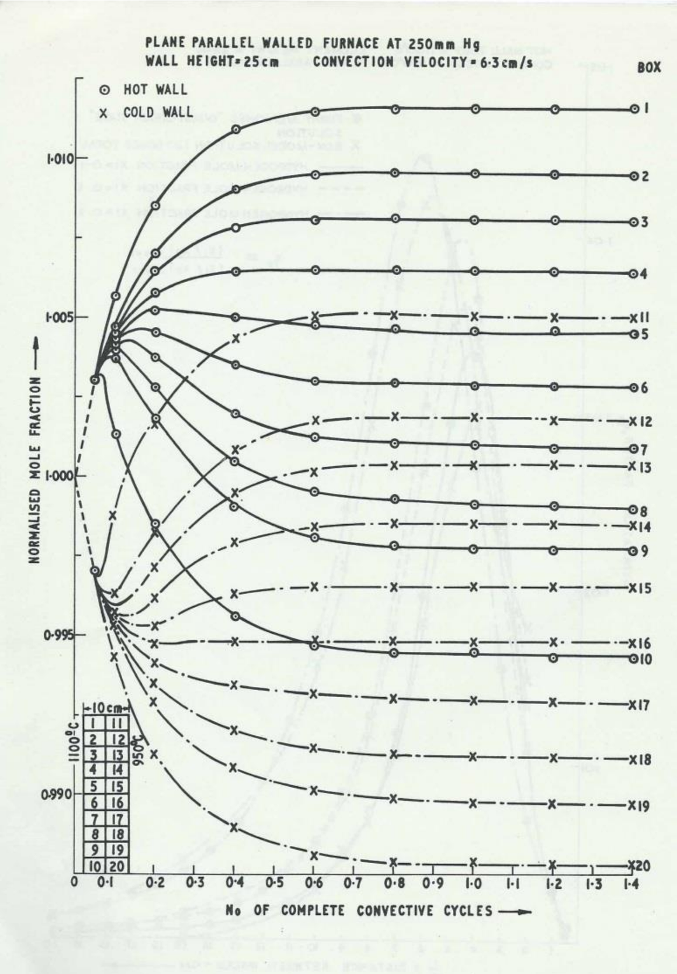


FIGURE 17. TRANSIENT APPROACH TO STEADY STATE (HYDROGEN MOLE FRACTION/ INITIAL VALUE i.e. 0·5)

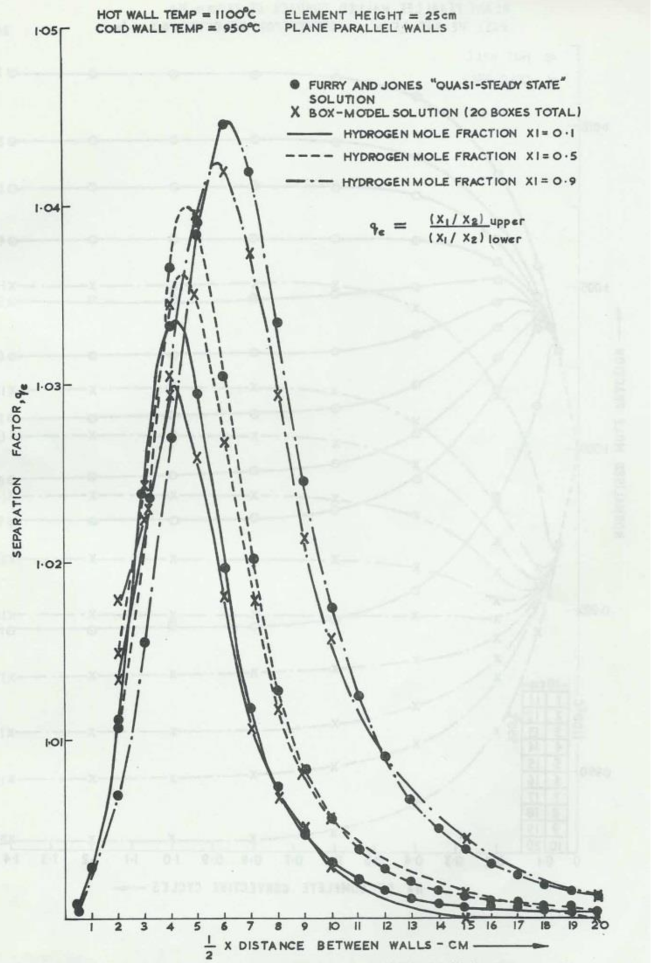


FIGURE 16. THE SEPARATION OF HYDROGEN (1)/METHANE (2) GAS MIXTURES AT 250mm Hg

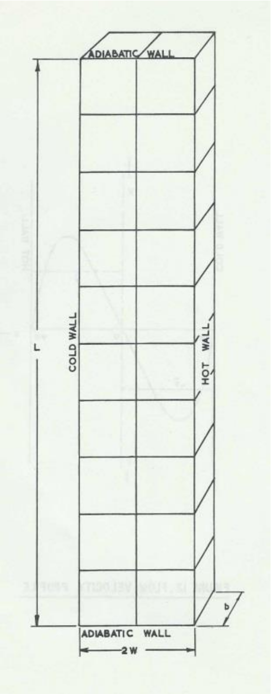


FIGURE 13. BOX MODEL

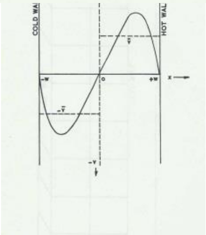
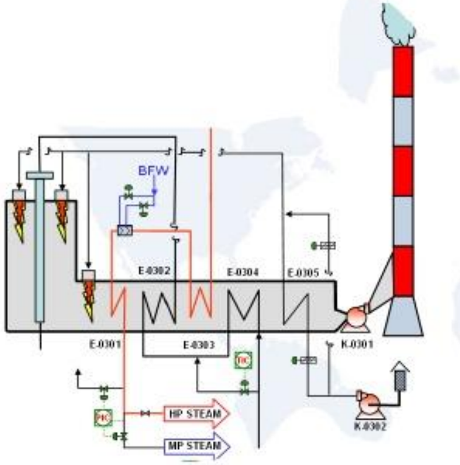
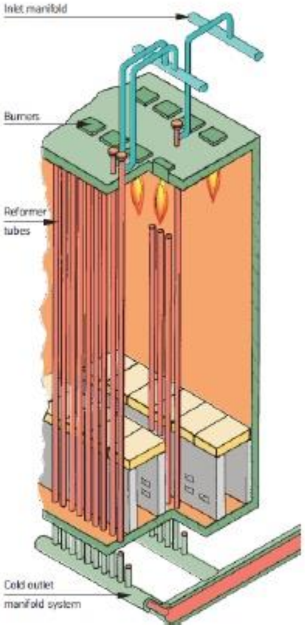


FIGURE 12. FLOW VELOCITY PROFILE

SOJOURN INTO HEAT TRANSFER AND AMMONIA

Heat Transfer
Kellogg International
Corporation
Baker Street

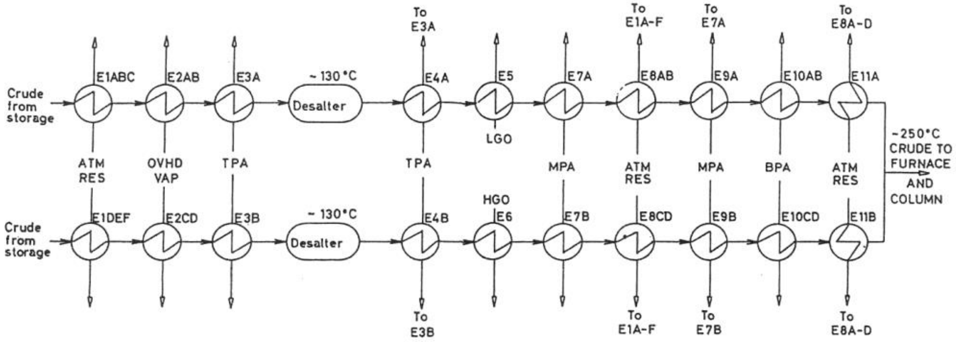


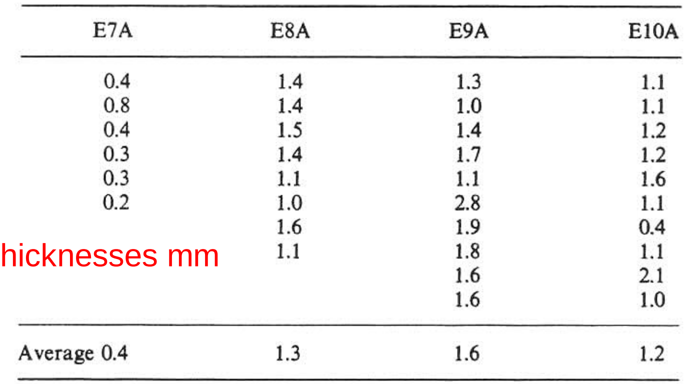


HEAT TRANSFER AND PRESSURE DROP PROBLEMS…

Consider a heat exchanger with 14.8 mm ID tubes with an overall heat transfer coefficient of 500 W/m^{2}K. A 1.0 mm layer of deposit builds up on the tube surface and it is found that the thermal conductivity of the deposit is 0.04 W/mK. By how much will the overall heat transfer coefficient have reduced?

If the pressure drop through this exchanger when clean was 1.0 bar what will the pressure drop have increased to if the mass flow rate through the exchanger is to be kept the same as when clean? (Assume that the surface roughness does not alter.)





Deposit thicknesses mm

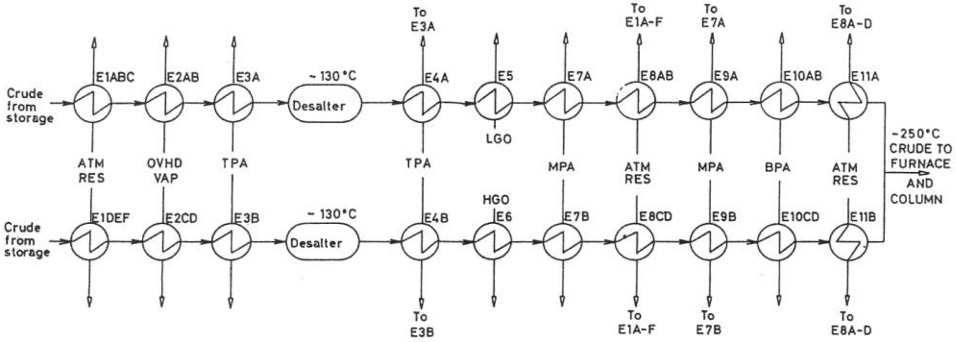
E7A	E8A	E9A	E10A
0.4	1.4	1.3	1.1
0.8	1.4	1.0	1.1
0.4	1.5	1.4	1.2
0.3	1.4	1.7	1.2
0.3	1.1	1.1	1.6
0.2	1.0	2.8	1.1
	1.6	1.9	0.4
	1.1	1.8	1.1
		1.6	2.1
		1.6	1.0
Average 0.4	1.3	1.6	1.2

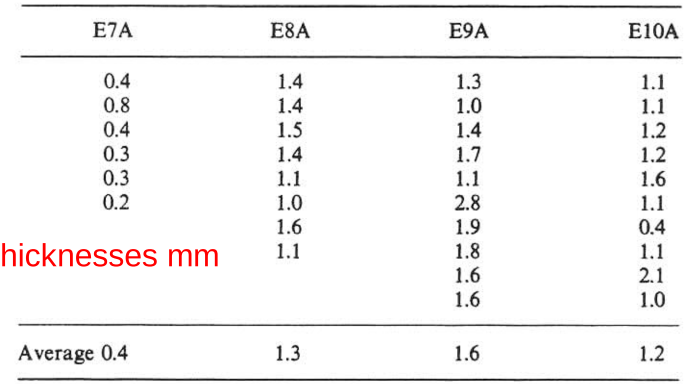
Crude oil preheat unit of 100,000 BPSD oil refinery

HEAT TRANSFER AND PRESSURE DROP PROBLEMS…

Consider a heat exchanger with 14.8 mm ID tubes with an overall heat transfer coefficient of 500 W/m^{2}K. A 1.0 mm layer of deposit builds up on the tube surface and it is found that the thermal conductivity of the deposit is 0.04 W/mK. By how much will the overall heat transfer coefficient have reduced? (Ans: by 93% to 37 W/mK)

If the pressure drop through this exchanger when clean was 1.0 bar what will the pressure drop have increased to if the mass flow rate through the exchanger is to be kept the same as when clean? (Assume that the surface roughness does not alter.) (Ans: doubled to about 2 bar)





	E7A	E8A	E9A	E10A
	0.4	1.4	1.3	1.1
	0.8	1.4	1.0	1.1
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	0.3	1.4	1.7	1.2
	0.3	1.1	1.1	1.6
	0.2	1.0	2.8	1.1
		1.6	1.9	0.4
		1.1	1.8	1.1
			1.6	2.1
			1.6	1.0
Average	0.4	1.3	1.6	1.2

Deposit thicknesses mm

Crude oil preheat unit of 100,000 BPSD oil refinery

…ARE EXPENSIVE

All fouling:

0.25% of GDP[1]

Crude oil fouling:

$1.2 billion in USA[2]

$4.5 billion in Western World[2]

10% of refinery carbon dioxide footprint[3]

Why:

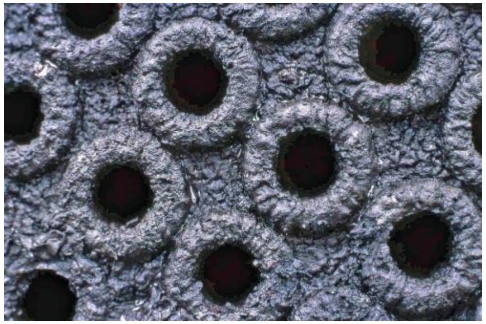
Reduced thermal efficiency, additional pressure drop (50% together), reduced or lost production, extra maintenance, extra surface area, cleaning, safety issues, etc

[1] Pugh S J, Hewitt G F and Muller-Steinhagen H 2007, Heat Exchanger Fouling & Cleaning VII, Proc. Int. Conf. on Heat Exchanger Fouling & Cleaning – Challenges & Opportunities, Tomar, Portugal, July 2007

[2] IHS ESDU, 2000, Fouling in the pre-heat train of a crude oil distillation unit, ESDU 00016, IHS ESDU International plc, London

[3] Muller-Steinhagen H, Malayeri M R and Watkinson A P, 2007, Heat Exchanger Fouling & Cleaning VII, Proc. Int. Conf. on Heat Exchanger Fouling & Cleaning – Challenges & Opportunities, Tomar, Portugal, July 2007

WHO WANTS TO GET THEIR HANDS DIRTY?



$$Q = UA\Delta T_{lm}$$

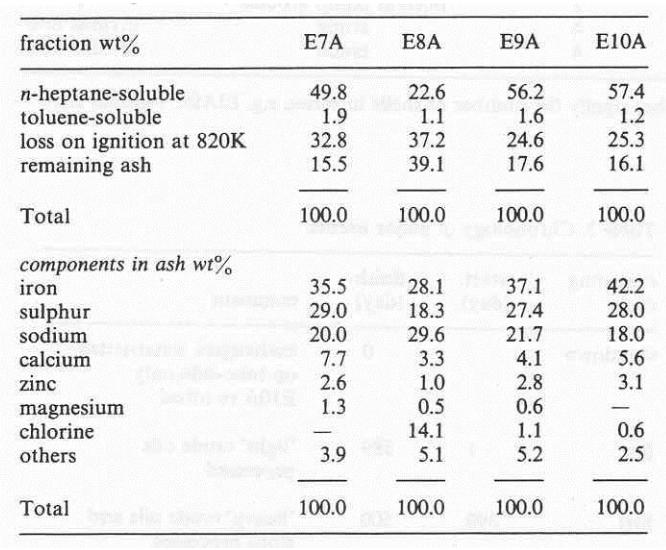
$$\Delta T_{lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{ln\frac{(T_1 - t_2)}{(T_2 - t_1)}}$$

$$\frac{1}{U_o} = \frac{1}{h_o} + \frac{1}{h_{od}} + \frac{d_o \ln(\frac{d_o}{d_i})}{2k_w} + \frac{d_o}{d_i}\frac{1}{h_{id}} + \frac{d_o}{d_i}\frac{1}{h_i}$$

$$R_f = \frac{1}{U_{t1}} - \frac{1}{U_{to}}$$

WHAT ARE THE DEPOSITS?

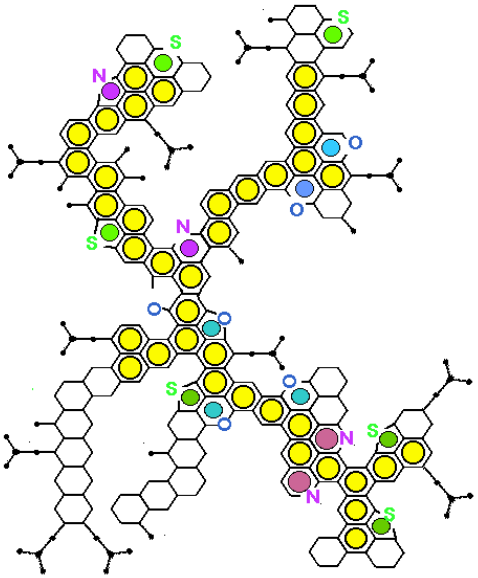
Mainly organic with some inorganic content. Typically contain organic polymers (eg asphaltenes), coke, particulates, inorganic salts, corrosion products, etc.



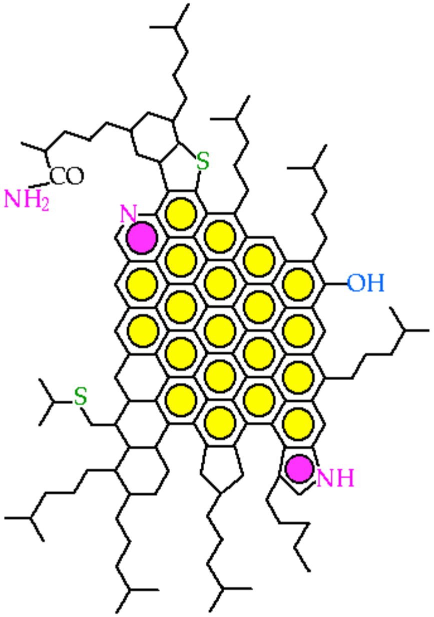
fraction wt%	E7A	E8A	E9A	E10A
n-heptane-soluble	49.8	22.6	56.2	57.4
toluene-soluble	1.9	1.1	1.6	1.2
loss on ignition at 820K	32.8	37.2	24.6	25.3
remaining ash	15.5	39.1	17.6	16.1
Total	100.0	100.0	100.0	100.0
components in ash wt%				
iron	35.5	28.1	37.1	42.2
sulphur	29.0	18.3	27.4	28.0
sodium	20.0	29.6	21.7	18.0
calcium	7.7	3.3	4.1	5.6
zinc	2.6	1.0	2.8	3.1
magnesium	1.3	0.5	0.6	—
chlorine	—	14.1	1.1	0.6
others	3.9	5.1	5.2	2.5
Total	100.0	100.0	100.0	100.0

Deposit analyses plant ↑ and laboratory ↓

Element	C	H	N	S	Fe
Crude A	36.12	4.11	<0.1	16.61	13.71
Crude B	53.98	6.11	0.48	13.82	7.53

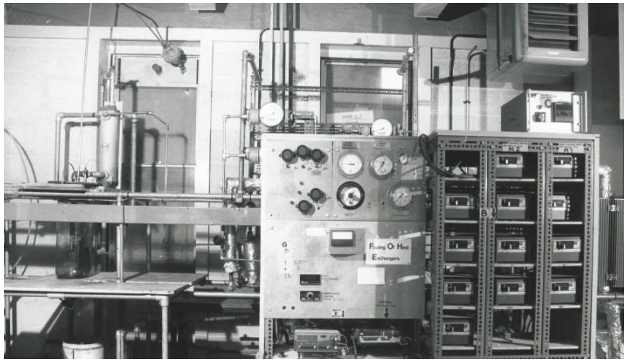


Archipelago structure in Maya (Mexico) crude



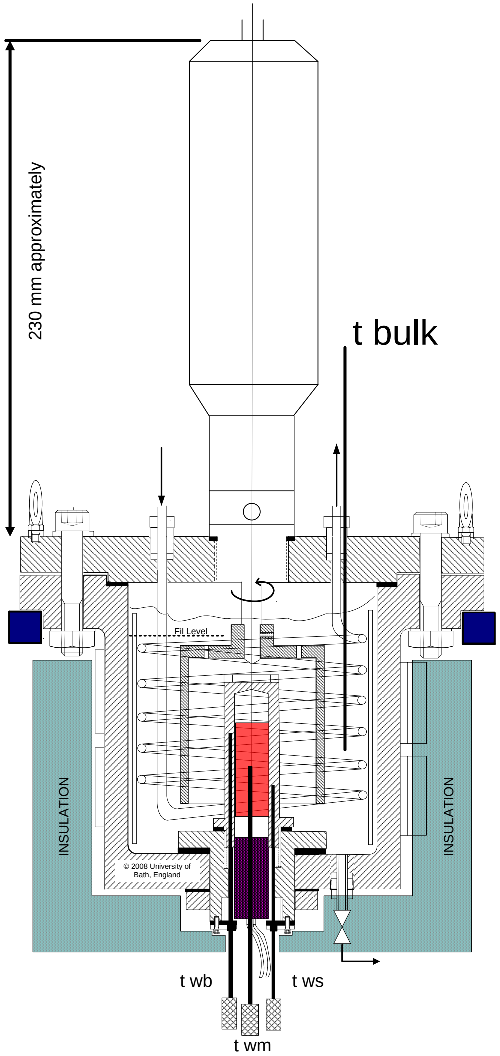
Continental structure in Venezuelan crude

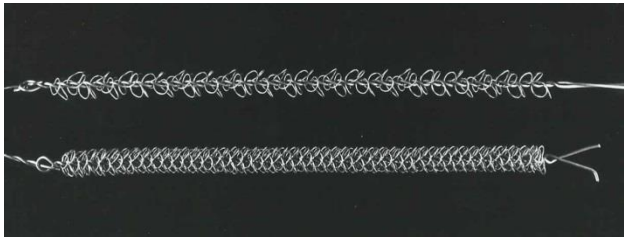
KEEP IT SIMPLE IN THE LABORATORY…

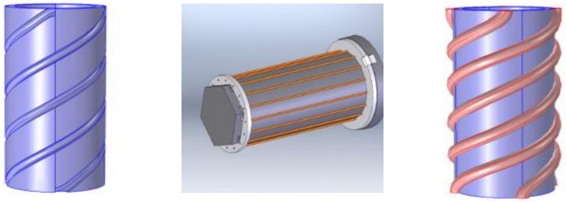


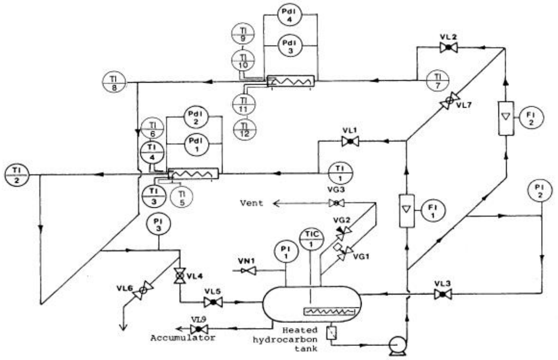
$$R_f = \left(\frac{T_s - T_b}{q}\right)_t - \left(\frac{T_s - T_b}{q}\right)_{t=0}$$

$$R_f = \left(\frac{T_{st} - T_{so}}{q}\right)$$

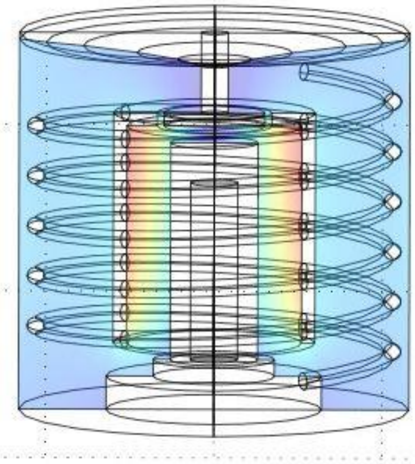




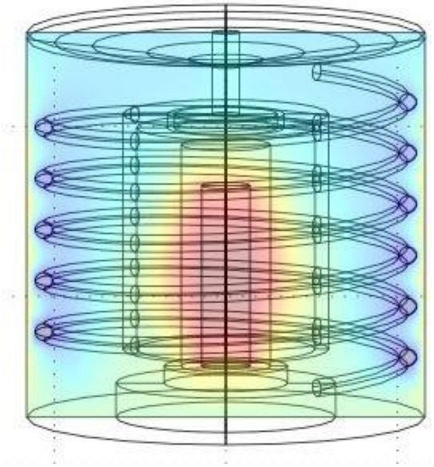




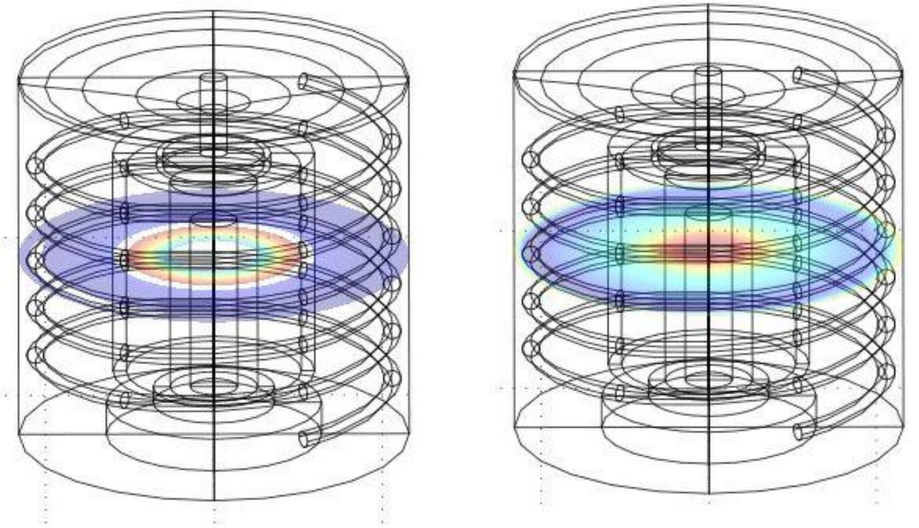
…AND LEAVE THE COMPLICATED STUFF TO CFD

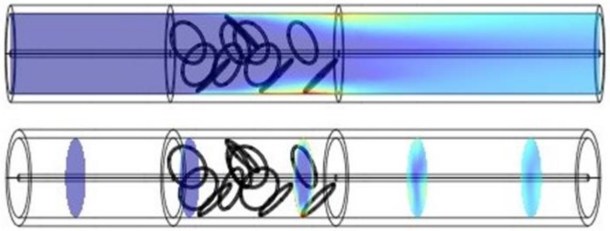


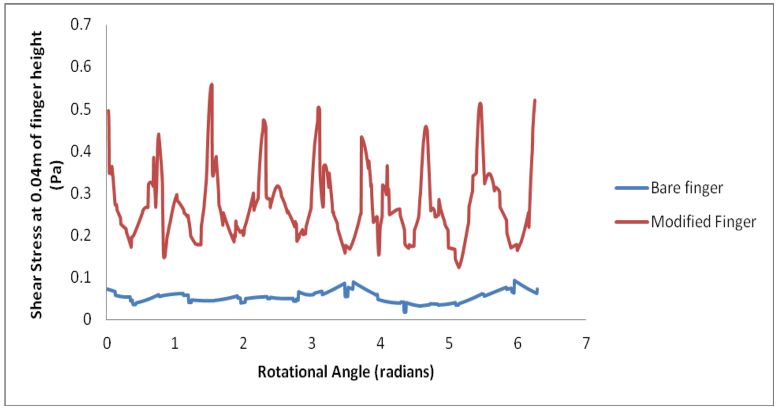
Velocity field

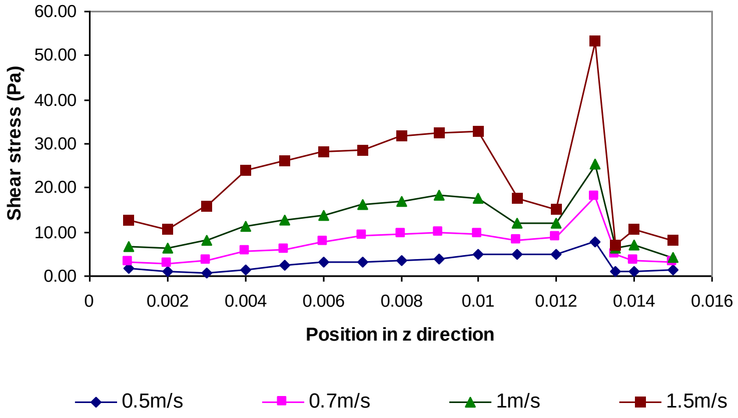


Temperature field



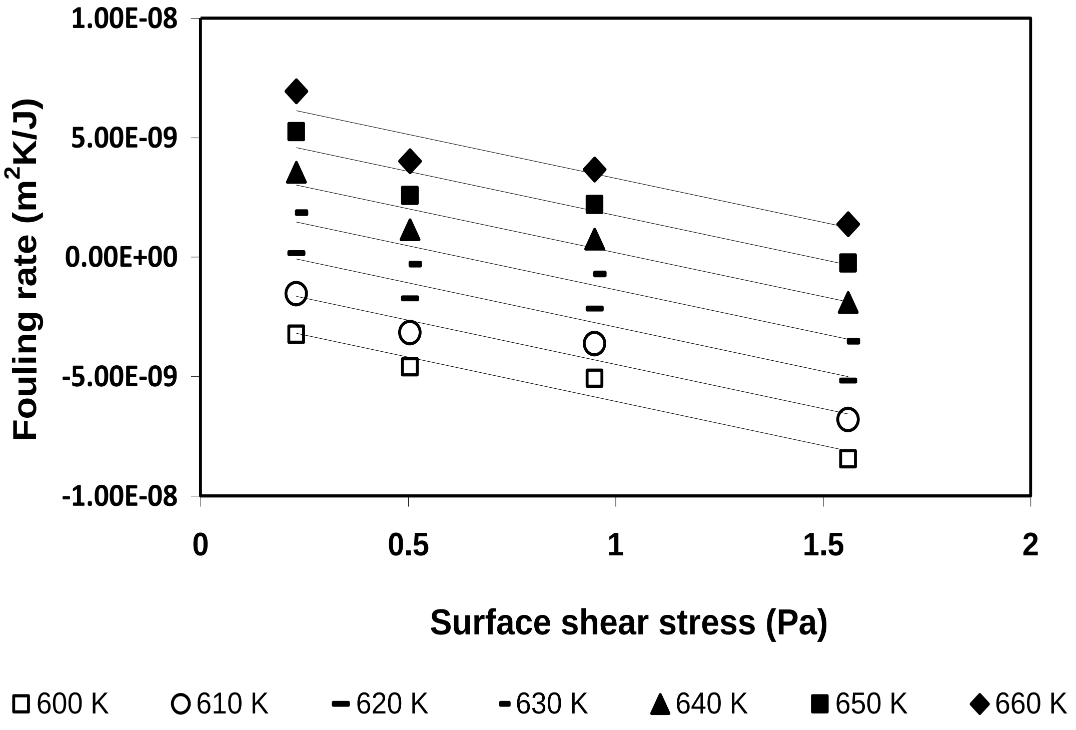




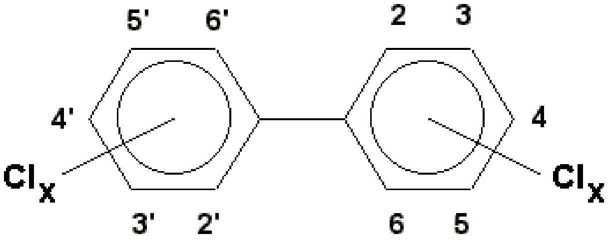


TWO RECENT ACHIEVEMENTS

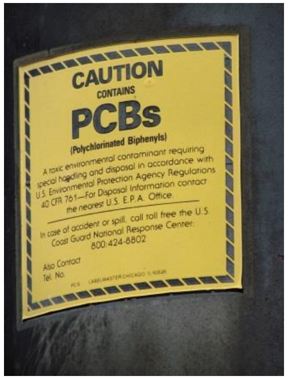
Equivalent velocity concept for complex geometries
Interpolation method to locate fouling thresholds



AN ACCIDENTALLY ARRANGED MEETING…



General formula for polychlorinated biphenyls



CAUTION

CONTAINS

PCBs

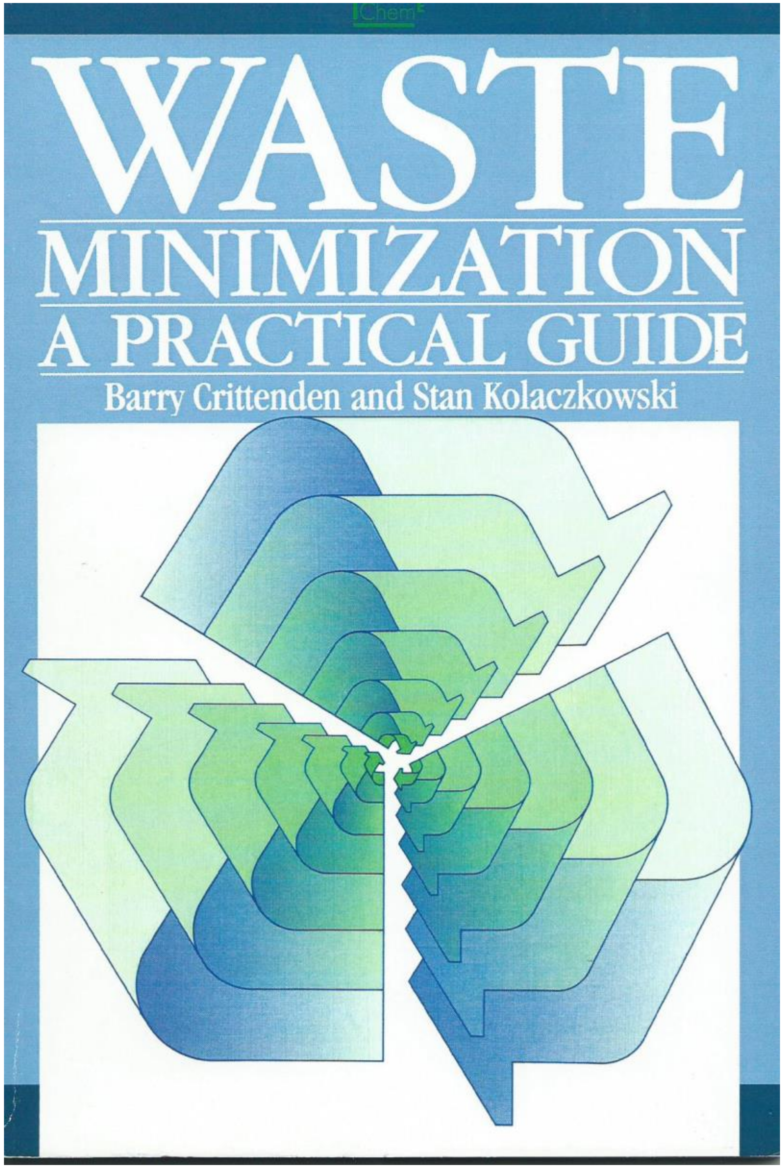
(Polychlorinated Biphenyls)

A toxic environmental contaminant requiring special handling and disposal in accordance with U.S. Environmental Protection Agency Regulations 40 CFR 761—For Disposal Information contact the nearest U.S. E.P.A. Office

In case of accident or spill, call toll free the U.S. Coast Guard National Response Center: 800-424-8802

Also Contact
Tel. No.

AN INVITATION…BUT NOT TO MAKE MONEY



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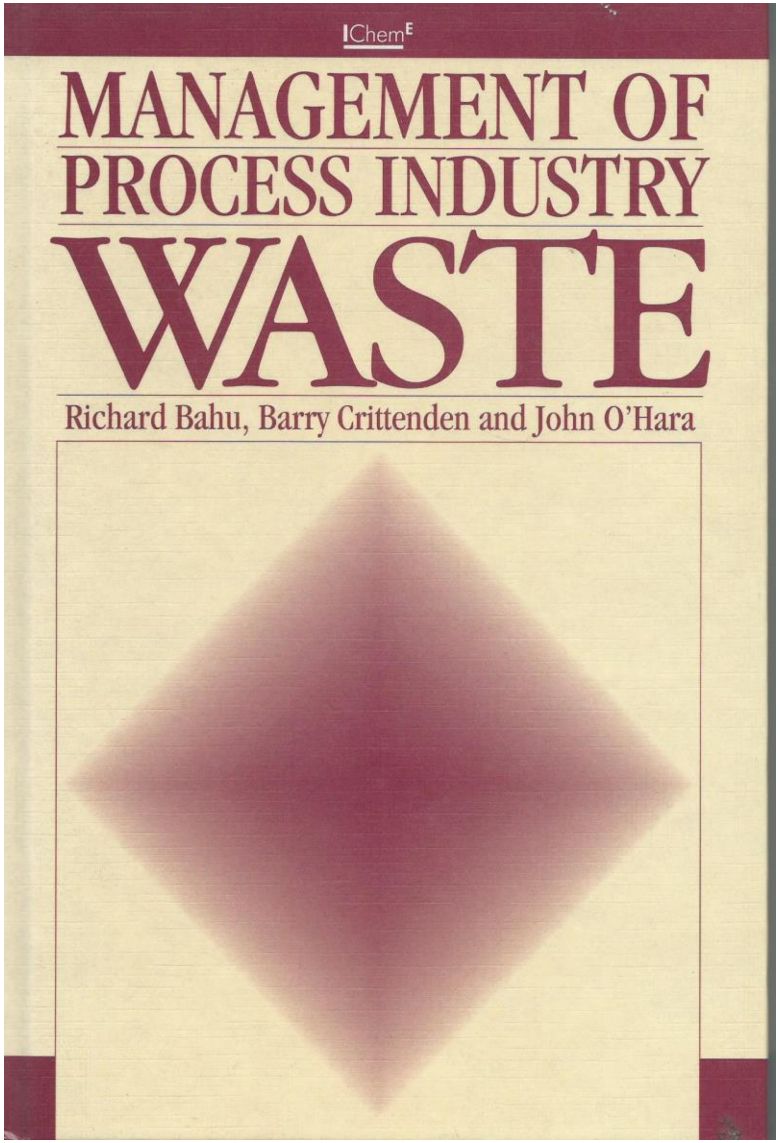
WASTE MINIMIZATION

A PRACTICAL GUIDE

Barry Crittenden and Stan Kolaczkowski

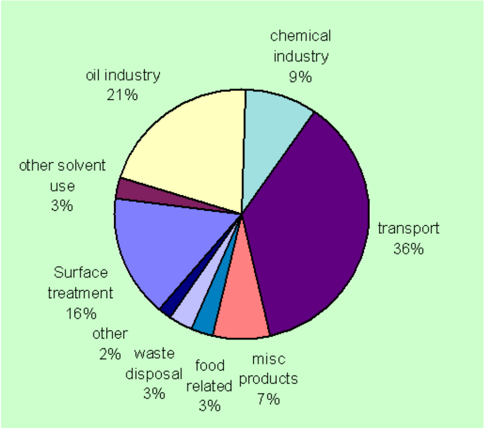


IChemE

MANAGEMENT OF PROCESS INDUSTRY WASTE

Richard Bahu, Barry Crittenden and John O'Hara

VOC EMISSIONS…A WORLD-WIDE ENVIRONMENTAL PROBLEM



UK GDP = 4.6% of global GDP (Scaruffi, 2004)

UK VOC emissions reduced to 1.5 million tonnes in 2002 (Environment Agency)

Worldwide VOC emissions therefore are approximately 32.6 million tonnes/year

Adsorption is used for 25% of total VOC control market (Frost & Sullivan, 2000)

Therefore about 8 million tonnes/year might be controlled by adsorption worldwide

A typical VOC concentration might be 2 g/m^3

Volume of air to be cleaned therefore could be 130,000 m^3/s

LEGISLATIVE DRIVERS

Gothenburg Protocol to Abate Acidification, Eutrophication & Ground-level Ozone (1999)

EU Solvent Directive (1999/13/EC)

EU Directive on National Emissions Ceilings (the NEC Directive 2001/81/EC)

EU Paints Directive (2004/42/CE)

and others

require the UK to reduce its VOC emissions to 1.2 million tonnes by 2010. Requirement will be met primarily through

UK Environmental Protection Act 1990 (EPA90)

UK Pollution and Prevention Control (England and Wales) Regulations 2000 (PPC Regulations)

REDUCE THE INVENTORY OF CARBON…

Granular activated carbons (GAC) have enjoyed a long and successful record in removing pollutants from aqueous and gaseous environments.

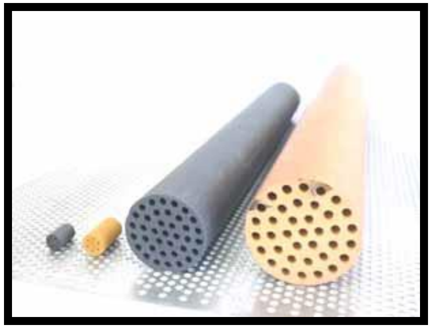
With pressures now to reduce energy demands and CO_2 emissions in all forms of processing, focus is shifting towards ways of operating AC systems at very much reduced pressure drops.

As an example, activated carbon monoliths (ACMs) can be used to remove volatile organic compounds (VOCs) from air streams with substantially reduced energy demands because (i) they have intrinsically low pressure drops, and (ii) they can be thermally cycled much faster than GAC and hence their carbon inventories can be reduced considerably.

Replace the large GAC bed with a much smaller volume of structured ACM →

MANUFACTURE OF ACMs

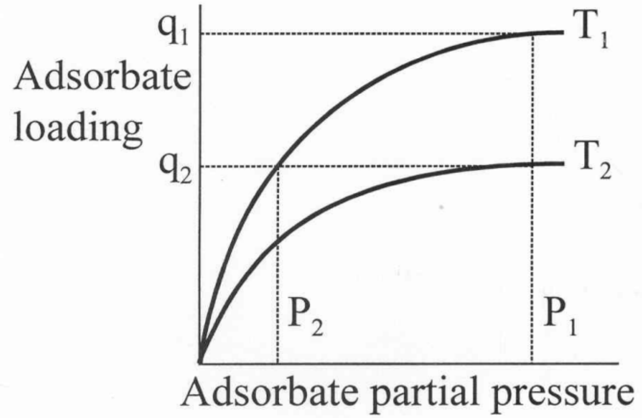
Gadkaree	Carbon from high carbon yield phenolic resin impregnated on ceramic honeycomb support	1998
Yates *et al.*	Activated carbon mixed with silicate clay before extrusion	2000
Tennison *et al.*	Binder-less activated carbon made from extruded phenolic Novolak resin	2001
Fuertes *et al.*	Carbon from phenolic Novolak resin mixed with Nomex fibres	2003
Valdés-Solis *et al.*	Carbon from phenolic Novolak resin dip-coated on ceramic support	2003



30% linear & 50% volumetric shrinkage on carbonisation

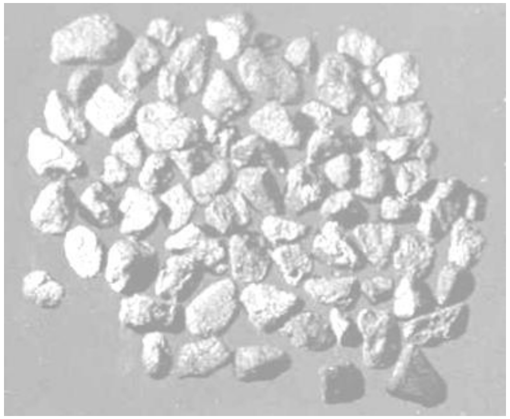
COMPARE AND CONTRAST

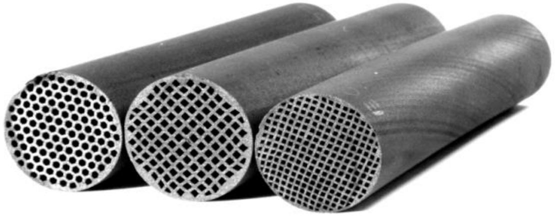
Granular activated carbon needs to be heated with steam or hot gas for its regeneration. This is a slow process, causing thermal swing adsorption (TSA) cycle times to be high, *eg* 8 hours. Recovery of the solvents is more difficult if steam is used although this is a good heating medium.

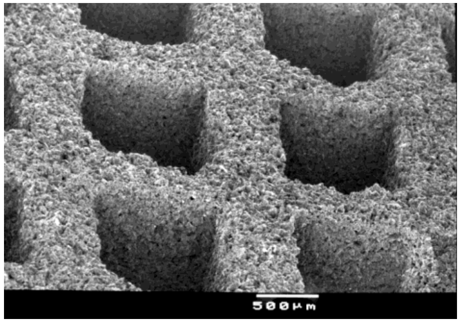


TSA pathway

COMPARE AND CONTRAST



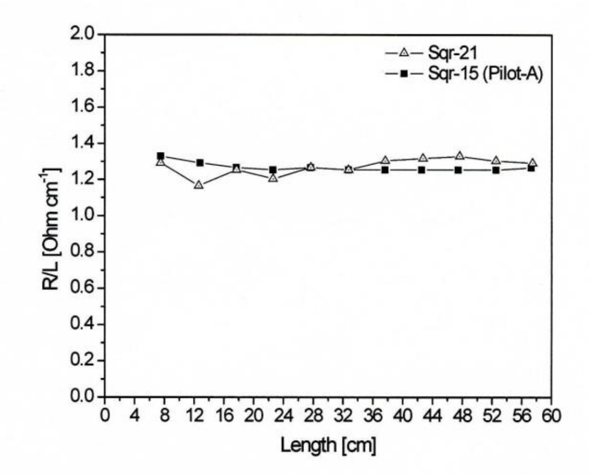


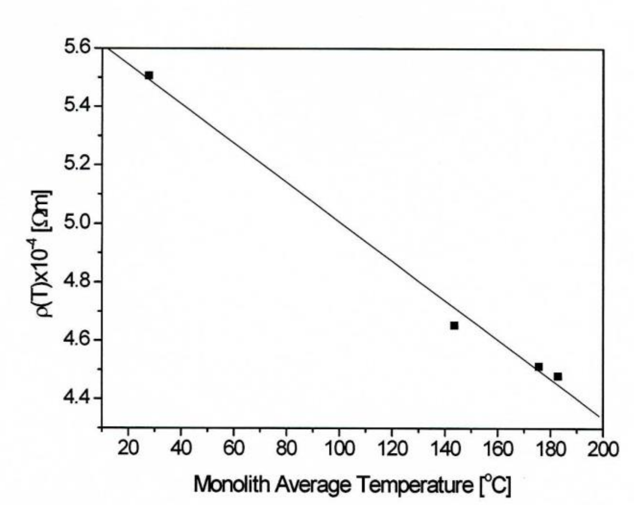


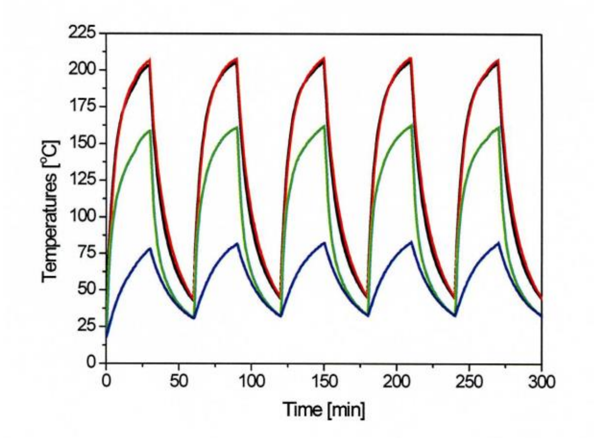
Granular activated carbon needs to be heated with steam or hot gas for its regeneration. This is a slow process, causing thermal swing adsorption (TSA) cycle times to be high, *eg* 8 hours. Recovery of the solvents is more difficult if steam is used although this is a good heating medium.

Activated carbon monoliths can be heated electrically at low potential difference. This is a fast process, thereby allowing operation at much shorter cycle times, *eg* 60 minutes. The consequence is that much less adsorbent is required and so the equipment is much smaller.

MONOLITH ELECTRICAL RESISTANCE

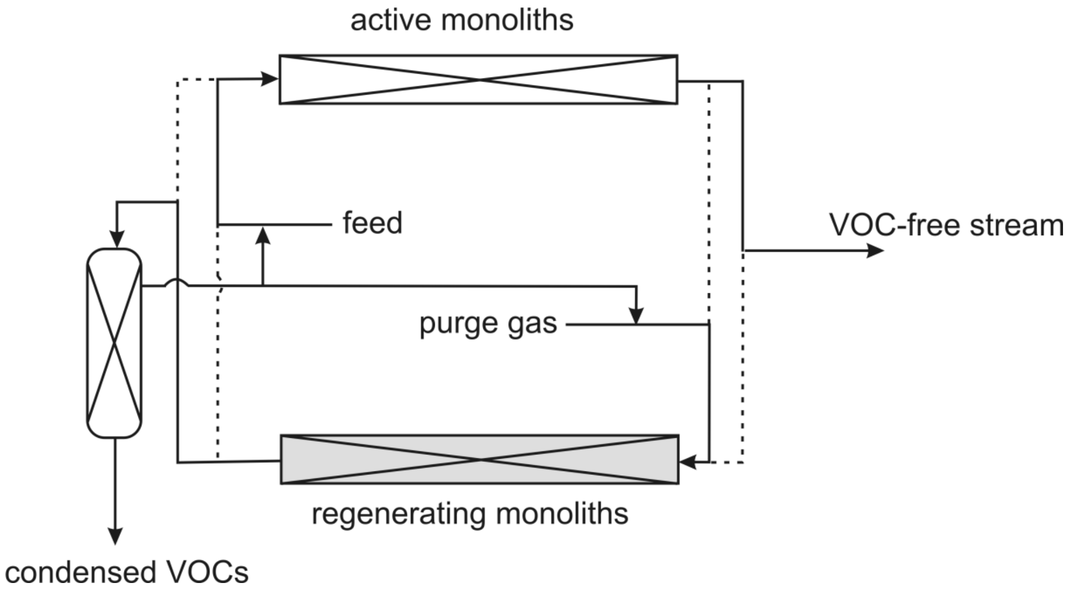






Electrothermal cycles of 30 mins heating and 30 mins cooling with 2 litres/min nitrogen (3 surface thermocouples)

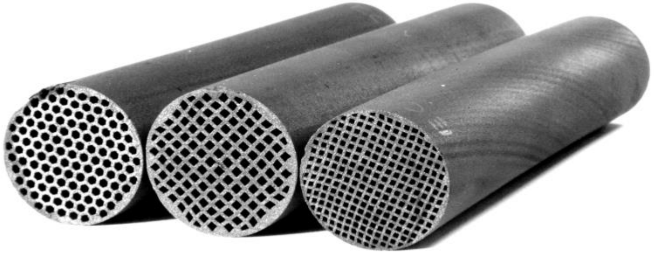
EXTRUDED ACMs IN VOC RECOVERY UNIT



Place R N, Blackburn A J, Tennison S R, Rawlinson A P and
Crittenden B D
“Method and equipment for removing volatile compounds from air”
US Patent 6964695 (2005), European Patent EP 1372917 (2008)

Winner – IChemE Severn Trent Water Safety Award 2002

COMPARE THE PRESSURE DROPS…



$$\frac{\Delta P}{L} = \frac{28.4 Q\mu}{a^4}$$

$$\frac{\Delta P}{L} = 150\frac{(1-e)^2}{e^3}\frac{\mu u}{d_p^2} + 1.75\frac{(1-e)}{e^3}\frac{\rho u^2}{d_p}$$

Skin friction only
(laminar flow)

Patton et al (2004)

Skin friction and form drag with the latter as a function of u^2 predominating

Ergun (1952)

BASIS OF PRESSURE DROP COMPARISON

Assume an average 20% loading (w/w) on both the granular and monolithic adsorbents (it has been shown that the kinetic performances of the two systems are quite similar).

Assume an 8.0 hour cycle time for granular (spherical) adsorbent.

Assume that the Ergun equation is applicable for the pressure drop through a bed of granular activated carbon (GAC).

Assume a 1.0 hour cycle time for monolith adsorbent.

Assume that the Poiseuille equation is applicable for the pressure drop for laminar flow through the monolith channels.

What is the potential benefit from switching from GAC to ACM for VOC control?

GLOBAL POTENTIAL

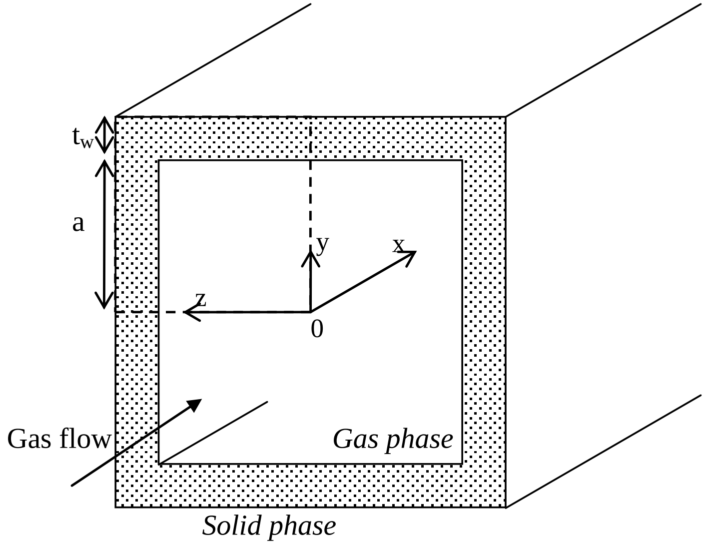
Pressure Drops for Worldwide Control of VOCs

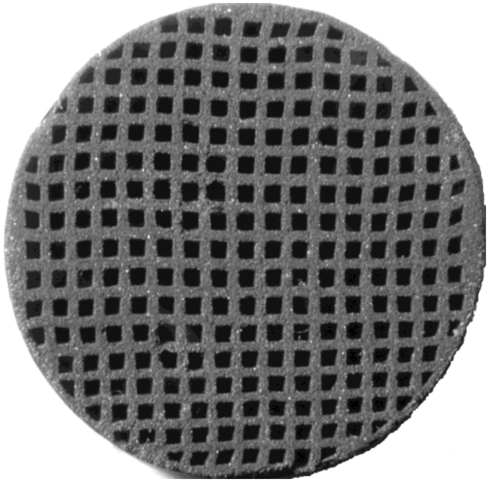
	Packed bed	**Monolith**
Pellet diameter, mm	1.0	-
Square channel monolith dimension, mm	-	0.63
Square channel monolith wall thickness, mm	-	0.43
Air flow rate, $m^3 s^{-1}$	130,000	130,000
Bed volume, m^3	50,000	6250
Reynolds number	100	157
Superficial velocity, $m s^{-1}$	1.55	1.55
Bed voidage or monolith fractional free volume	0.4	0.4
f_p or f_m	49.7	0.41
Bed cross sectional area, m^2	83,870	83,870
Bed length, m	0.60	0.075
Pressure gradient, $N m^{-3}$	70,747	5790
Pressure drop, $N m^{-2}$	42,450	434
Power requirement, MW	5500	56

Potential power saving is substantial.

Potential for CO_2 reduction depends on energy sources.

FUNDAMENTAL DESIGN





Decisions:

3D diffusion & convection in the channel gas phase

Various flow regimes in the channels (*eg* plug, axially dispersed plug, fully developed, developing)

3D diffusion in the solid phase

Adsorption at the gas-solid interface (*eg* Langmuir, Tóth)

Isotropic, anisotropic solid phase

Isothermal, non-isothermal

Uniform, non-uniform channels

FLOW AND CONVECTION

Mass balance gas phase:

$$\frac{\partial c}{\partial t}-D_M\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right)+u_{ave}\frac{\partial c}{\partial x}=0$$

Mass balance solid phase:

$$\frac{\partial q}{\partial t}=D_{eff}\left(\frac{\partial^2 q}{\partial x^2}+\frac{\partial^2 q}{\partial y^2}+\frac{\partial^2 q}{\partial z^2}\right)$$

Tóth model:

$$q=q_{max}\frac{bp}{\left[1+(bp)^n\right]^{1/n}}$$

Energy balance gas phase:

$$\rho_g c_{pg}\frac{\partial T_g}{\partial t}-\lambda_g\left(\frac{\partial^2 T_g}{\partial x^2}+\frac{\partial^2 T_g}{\partial y^2}+\frac{\partial^2 T_g}{\partial z^2}\right)+\rho_g c_{pg}u(y,z)\left(\frac{\partial T_g}{\partial x}+\frac{\partial T_g}{\partial y}+\frac{\partial T_g}{\partial z}\right)=0$$

Energy balance solid phase:

$$\rho_s c_{ps}\frac{\partial T_s}{\partial t}-\lambda_s\left(\frac{\partial^2 T_s}{\partial x^2}+\frac{\partial^2 T_s}{\partial y^2}+\frac{\partial^2 T_s}{\partial z^2}\right)=0$$

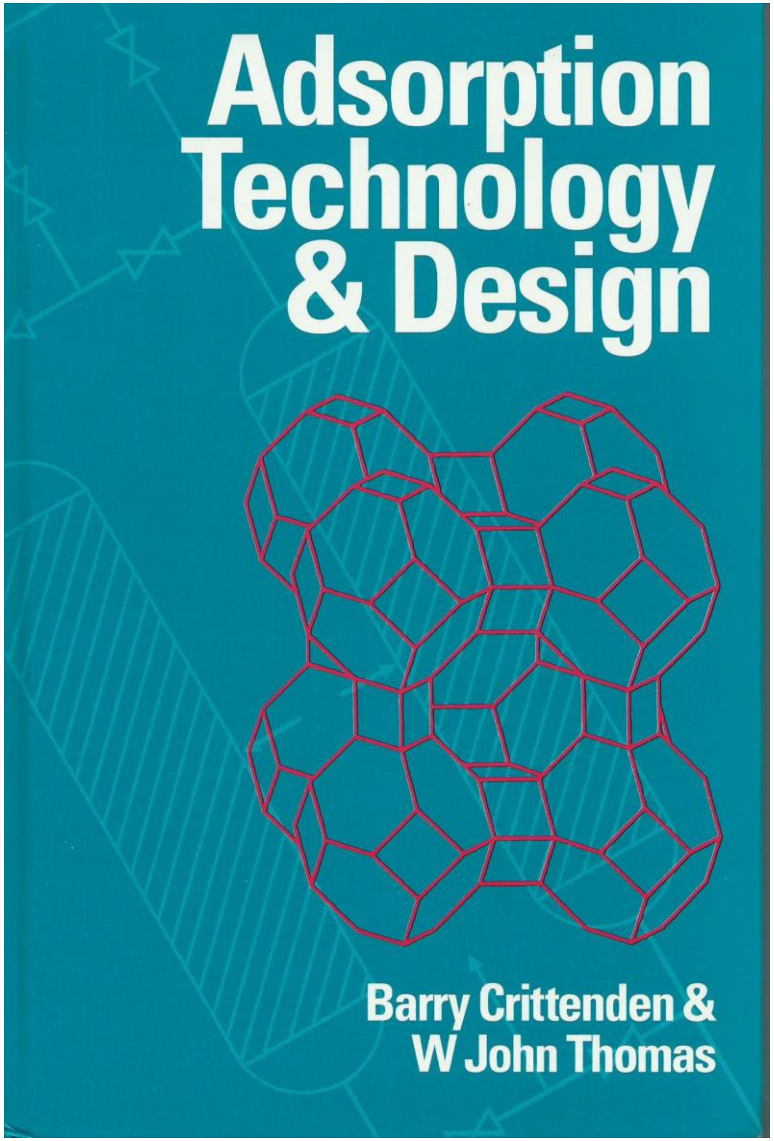
Energy balance interface:

$$\lambda_s\left.\frac{\partial T_s}{\partial z}\right|_{z=a^+}=\Delta H\frac{d\bar{q}}{dt}+\alpha_g A\left(T_s-T_0\right)$$

Gas channel heat transfer coefficient:

$$Nu=\frac{hd_{ch}}{\lambda_g}=2.977\left(1+0.095\frac{d_{ch}}{L}Re\ Pr\right)^{0.45}$$

…STILL DO NOT MAKE MUCH MONEY FROM PUBLISHING



AND FINALLY…BLACK POWDER?

Sulphur + charcoal + potassium nitrate

INNOCENT ANGLER

CHARCOAL, SULPHUR & SALTPETRE IS ON THE WAY…

FINALLY…BACK TO THE BEGINNING