ACTIVATED CARBON
CHARACTERISTICS-PERFORMANCE-REGENERATION

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ACTIVATED CARBON

- BEST BROAD SPECTRUM *ADSORBENT* FOR POLLUTION CONTROL (GAS & LIQUID PHASES)
- *GAS PHASE* - SOLVENT RECOVERY, GAS SEPARATIONS, NERVE GASES
- *LIQUID PHASE* - MINERAL RECOVERY, SURFACTANT REMOVAL, DE-CHLORINATION, WATER-WASTEWATER TREATMENT
- ALL *COMERCIALLY ACTIVATED CARBONS* VARY CONSIDERABLY IN ADSORPTION CHARACTERISTICS FOR A GIVEN POLLUTANT

ACTIVATED CARBON ***CHARACTERISTICS***

- A “SOLID SPONGE”
- INTERNAL SURFACE AREA (700 -1,200 m^2/gm)
- PORE DIAMETERS
    - micropores - <40 A
    - mesopores - 40-5,000 A
    - macropores - 5,000 -20,000 A
- LIQUID & GAS PHASE CARBONS

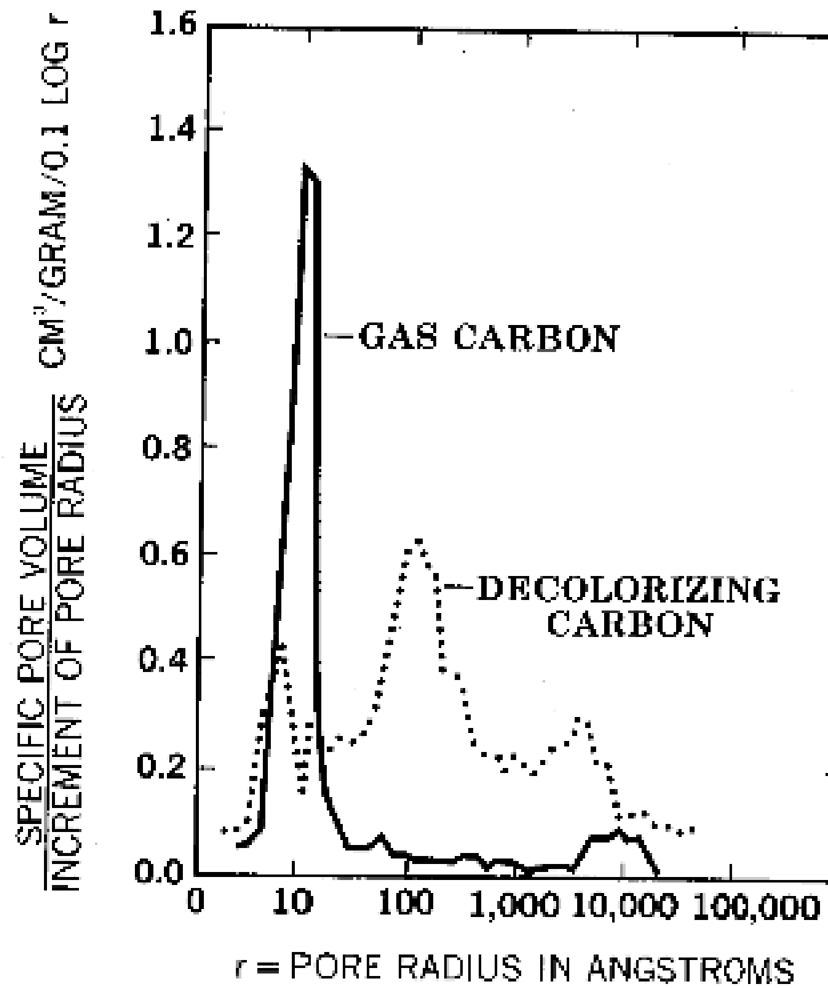


Figure 1. Pore volume distributions of typical gas and liquid phase activated carbons

MANUFACTURING PROTOCOLS AFFECT AC PROPERTIES

- *SOURCE MATERIAL* - COAL, LIGNITE, WOOD, COCONUT SHELL, and PETROLEUM RESIDUES
- *TIME ,TEMPERATURE & OXIDIZING GAS*
- *PORE SIZE & VOLUME DISTRIBUTIONS*
- *SURFACE CHEMISTRY* - oxygen complexes, (ether,peroxide, carboxyl, quinones, etc)

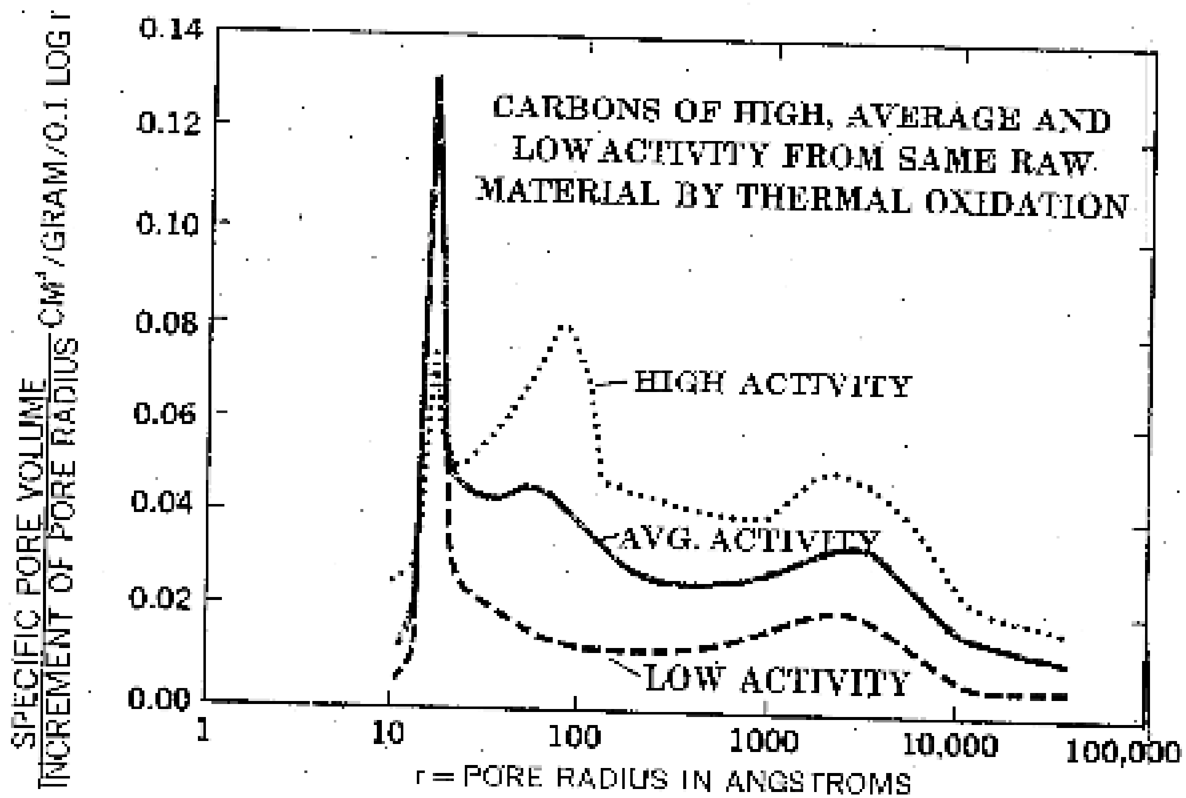


Figure 2 Pore volume distributions of typical decolorizing (liquid) activated carbons

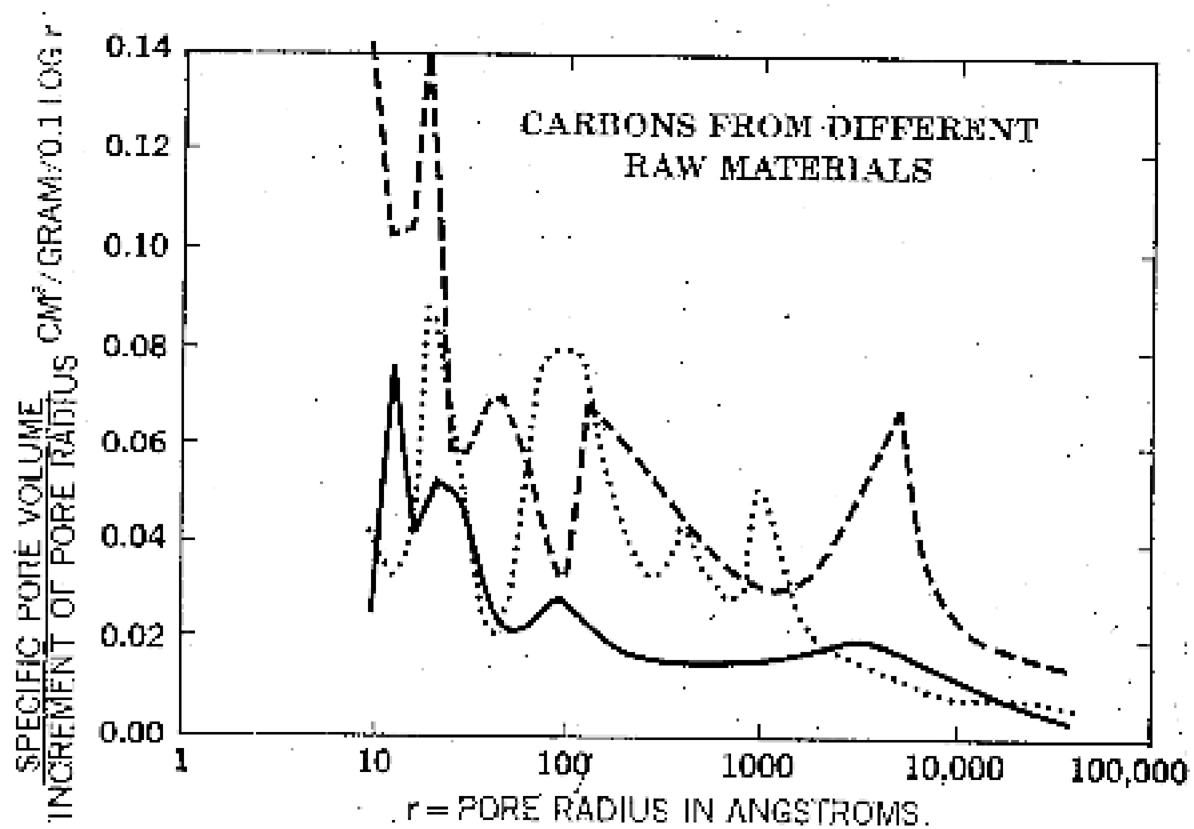


Figure 3 Pore volume distributions of typical decolorizing (liquid) activated carbons

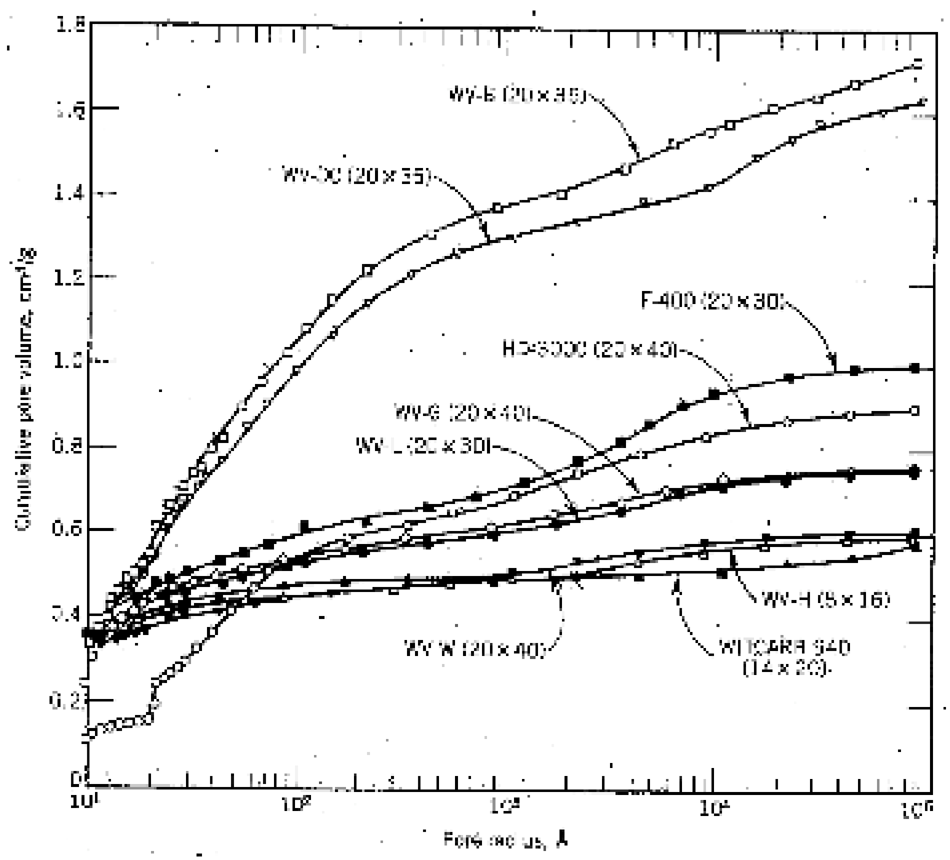


Figure 4 Pore size distributions for various commercially available activated carbons

Activated Carbon (Mesh Size)	Manufacturer	Raw Material	Surface Area (m^2/g)		Pore Volume (cm^3/g)	
			BET	Macro-pore	Macro-pore	Total
Filtrasorb 400 (<14)	Calgon Corp.	Bituminous coal	1228	366	0.625	1.108
Filtrasorb 400 (20 × 30)	Calgon Corp.	Bituminous coal	1075	309	0.643	1.071
Filtrasorb 400 (40 × 60)	Calgon Corp.	Bituminous coal	1155	433	0.847	1.235
Hydrodarco 3000 (20 × 40)	ICI America	Lignite coal	575	99	0.787	0.975
Witcarb 940 (14 × 20)	Witco Chemical Corp.	Petroleum-based coke	950	106	0.208	0.599
Nuchar WV-B (20 × 35)	Westvaco	Bituminous coal	1422	778	1.290	1.865
Nuchar WV-DC (20 × 35)	Westvaco	Wood-based coal	1115	621	1.230	1.764
Nuchar WV-G (20 × 40)	Westvaco	Bituminous coal	1020	238	0.398	0.814
Nuchar WV-H (8 × 16)	Westvaco	Bituminous coal	910	133	0.251	0.610
Nuchar WV-L (20 × 30)	Westvaco	Bituminous coal	976	188	0.420	0.818
Nuchar WV-W (20 × 40)	Westvaco	Bituminous coal	861	154	0.281	0.612

Table 1 Characteristics of selected activated carbons

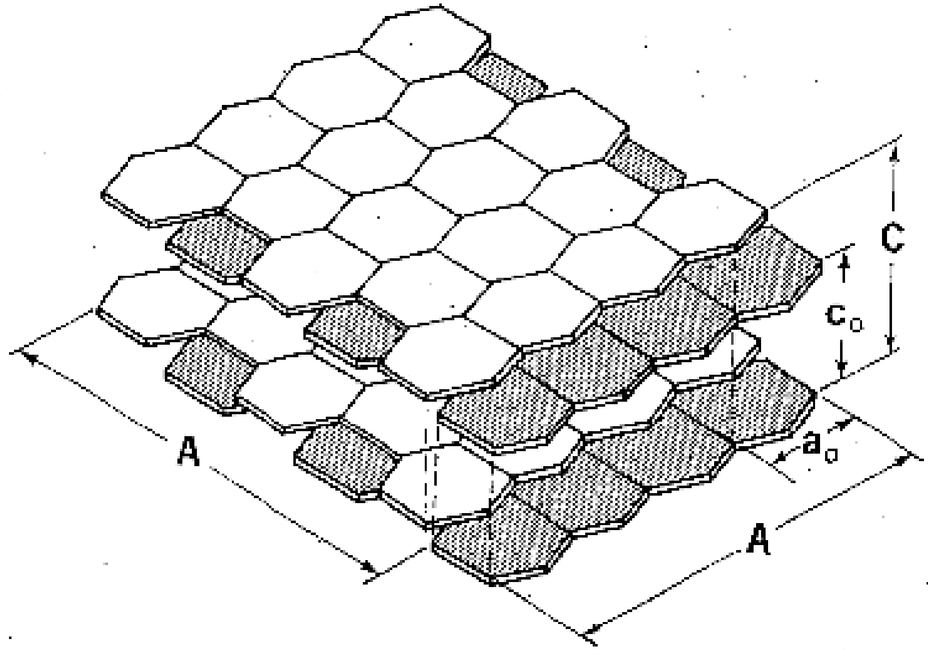


Figure 5 Crystallite showing dimensions

SAMPLE	a_o	c_o	A	C
DARCO S-51	2.45	7.20	27	9.5
DARCO G-60	2.45	7.50	38	9.5
DARCO K	2.45	7.30	27	10.7
Competitive	2.45	7.70	30	10.0
Graphite	2.456	6.708	>1000	>1000

Table 2 Crystallite sizes in angstroms

ADSORPTION

- ACCUMULATION OF SUBSTANCES AT A PHASE BOUNDRY BETWEEN TWO PHASES
- *ADSORBATES* ARE SUBSTANCES ACCUMULATED BY AN *ADSORBENT*
- ***PHYSICAL ADSORPTION*** - WEAK *VAN DER WAALS FORCES,* REVERSIBLE PROCESS
- ***CHEMISORPTION -*** REACTION WITH AC SURFACES, IRREVERSIBLE PROCESS, SURFACE CHEMISTRY

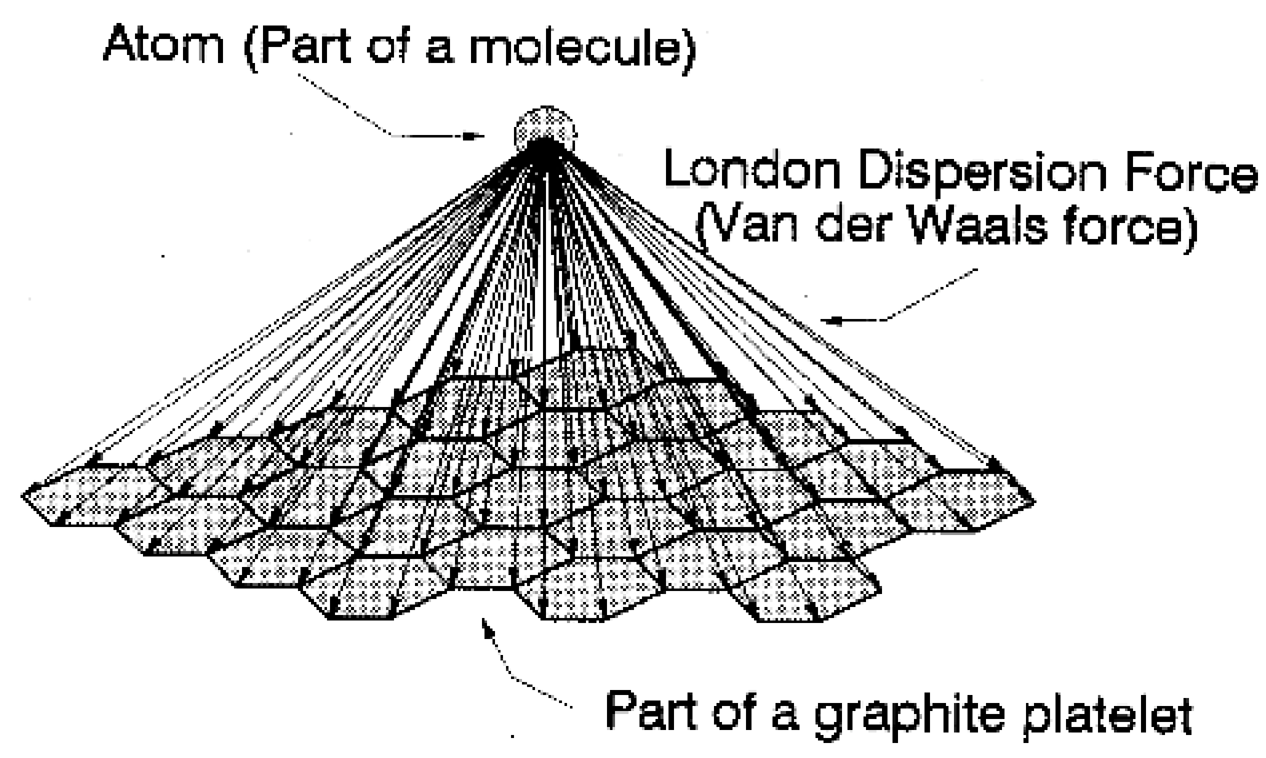


Figure 6 Van der Waals forces in adsorption

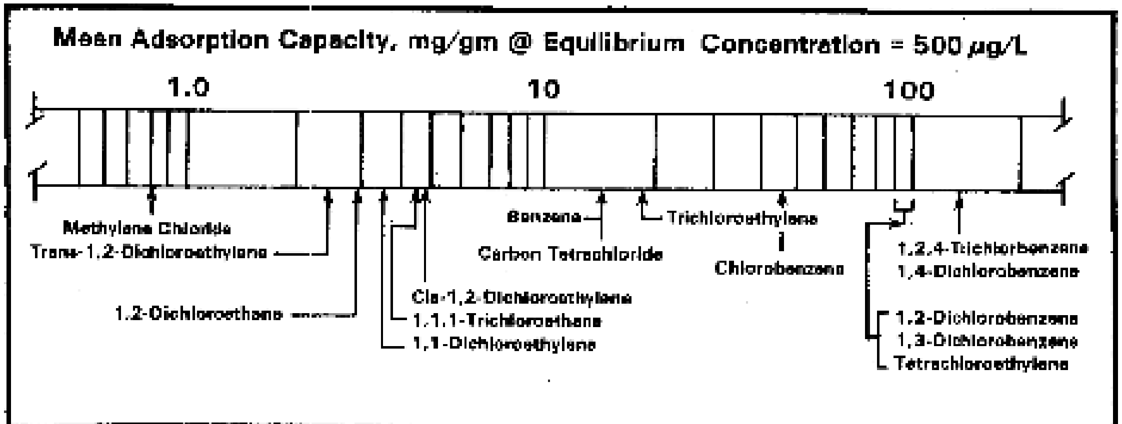
AC *PERFORMANCE*

- READILY ADSORBED ORGANICS

  AROMATIC SOLVENTS, CHLORINATED AROMATICS, CHLORINATED ALIPHATICS, PHENOLS, HIGH MOLECULAR WEIGHT HYDROCARBONS

- POORLY ADSORBED ORGANICS

  ALCOHOLS, LOW MOLECULAR WEIGHT ALDEHYDES, KETONES AND ACIDS, LOW MOLECULAR WEIGHT ALIPHATICS, VERY HIGH MOLECULAR WEIGHT ALIPHATICS



	Freundlich Parameters K	1/n
Benzene	1.0	1.6*
	16.6	0.4**
	49.3	0.6†
	29.5	0.4††
	14.2	0.4§
Carbon Tetrachloride	11.1	0.8*
	28.5	0.8†
	38.1	0.7**
	25.8	0.7††
	14.2	0.7§
	14.8	0.4§§
Chlorobenzene	91.0	1.0*
1,2-dichlorobenzene	129.0	0.4*
1,3-dichlorobenzene	118.0	0.4*
1,4-dichlorobenzene	121.0	0.6*
	228.0	0.4**
1,2-dichloroethane	3.6	0.8*
	5.7	0.5§§
cis-1,2-dichloroethylene	8.4	0.5§§
	6.5	0.7‡

	Freundlich Parameters K	1/n
trans-1,2-dichloroethylene	3.1	0.5*
1,1-dichloroethylene	4.9	0.5*
Methylene chloride	1.3	1.2*
	1.6	0.7***
Tetrachloroethylene	50.8	0.6*
	84.1	0.4§§
	273.0	0.6***
1,2,4-trichlorobenzene	157.0	0.3*
1,1,1-trichloroethane	2.5	0.3*
	9.4	0.5§§
Trichloroethylene	28.0	0.6*
	26.2	0.5†
	28.2	0.4§§
Vinyl chloride	Not Reported	

Freundlich equation:
$x/m(mg/gm) = K\,C_e(mg/l)^{1/n}$

*Filtrasorb® 300(40) §Hydrodarco® 1030 (62) †Norit(62)
**Filtrasorb® 400(62) §§Witcarb® 950 ††Nuchar® WV-G(62)
***Filtrasorb® 400(47) ‡Filtrasorb® 300

Figure 7 Comparison of isotherm adsorption capacities

AC THERMAL ***<u>REGENERATION</u>***

MULTIPLE HEARTH FURNACES

ROTARY KILNS

FLUIDIZED BEDS

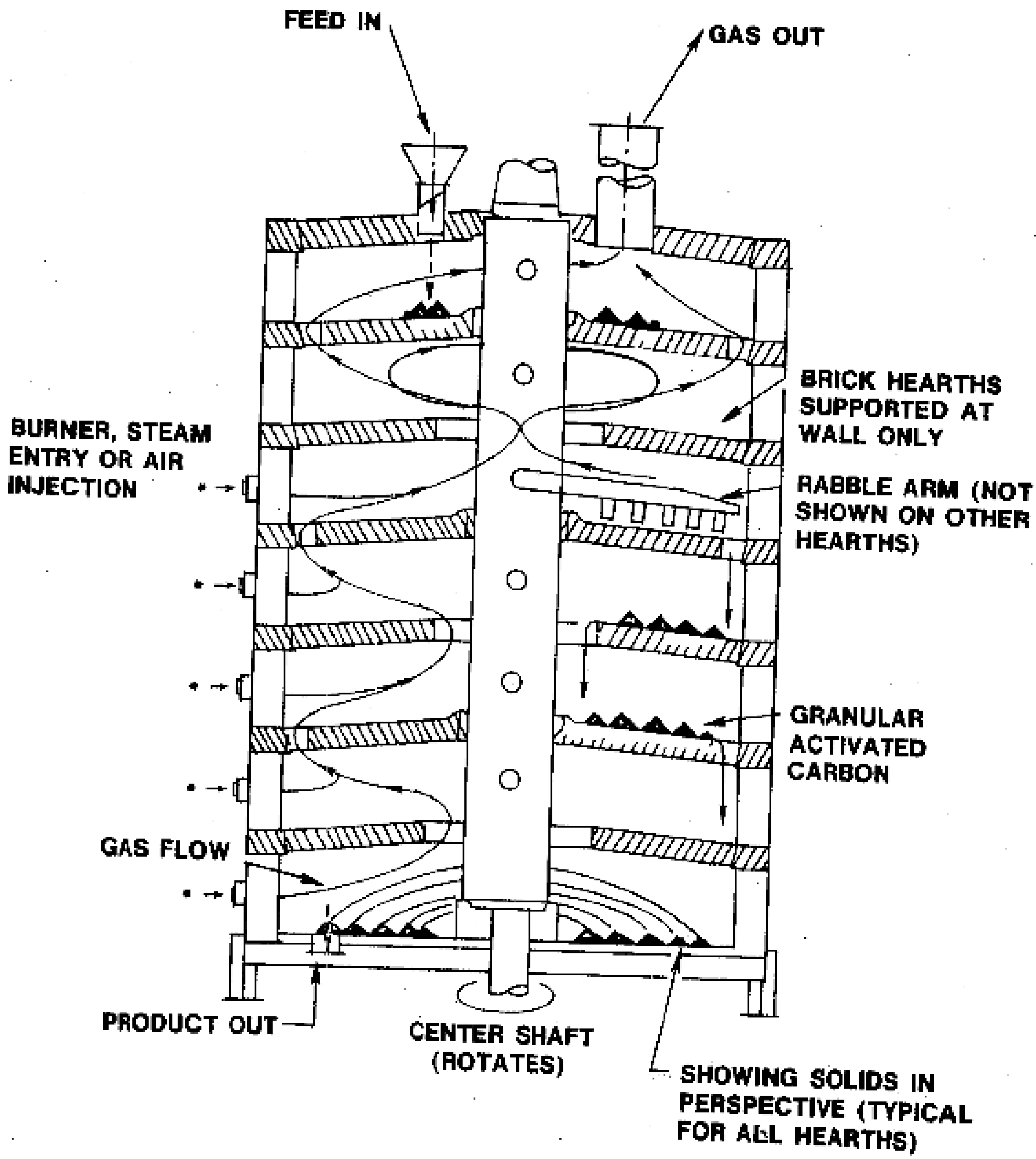


Figure 8 Cross-section of a multi-hearth furnace

TYPICAL AC PROPERTY CHANGES WITH REGENERATION

CYCLE	ASH %	I_2 #	DENSITY
initial	5.7	1090	0.469
1	7.6	1040	0.468
2	8.6	935	0.469
3	9.5	940	0.473

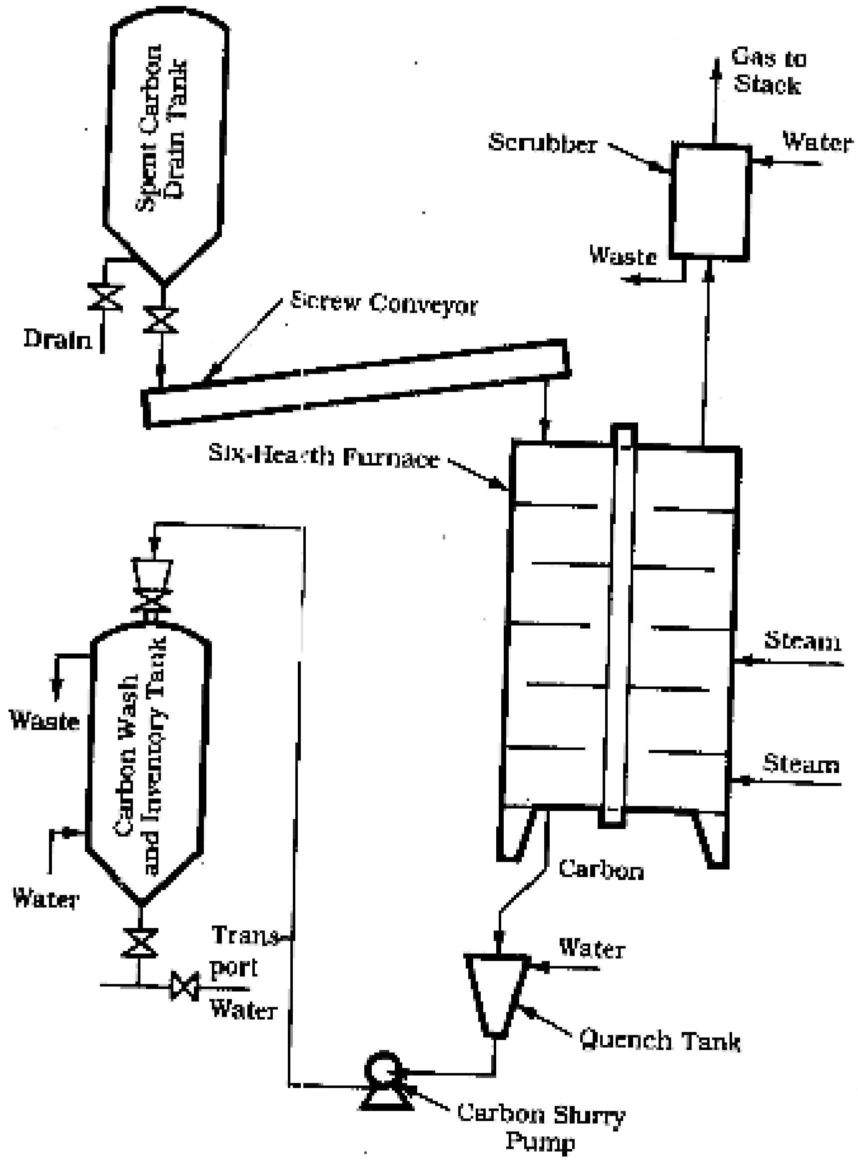


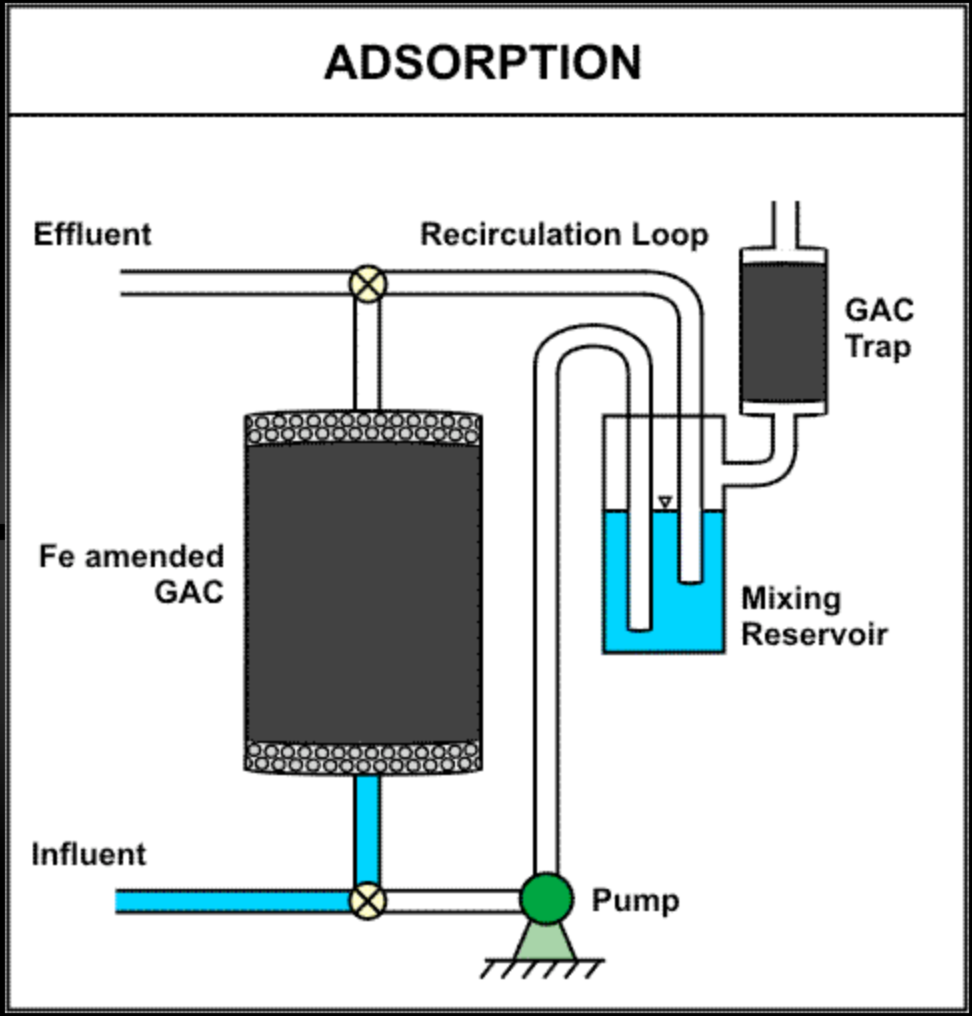
Figure 9 Typical activated carbon thermal regenerating facility

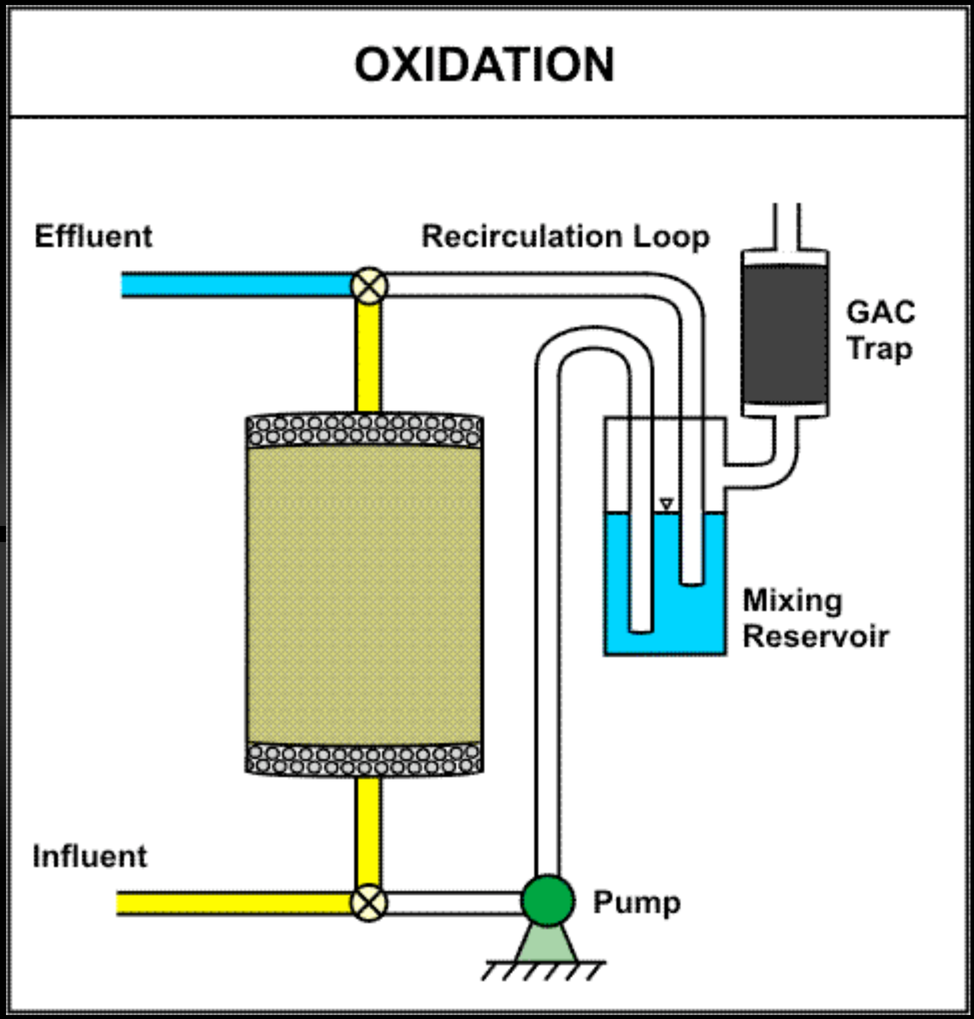
THERMAL REGENERATION

- 10% - 15% MASS LOSS PER REGENERATION CYCLE
- PARTICLE SIZE CHANGES
- REGENERATED AC IS A NOT 100% FROM THE OWNERS BATCH

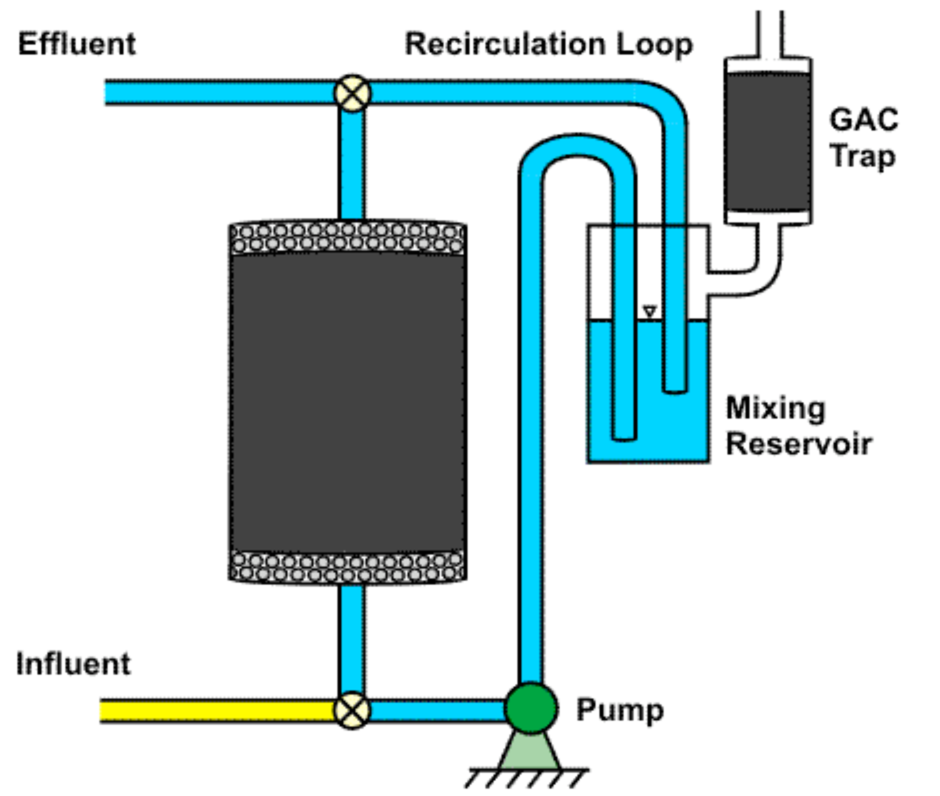
Fenton-driven Regeneration of GAC

- ✓ Transform environmental contaminants into less toxic byproducts
- ✓ Re-establish the sorptive capacity of the GAC for the target chemicals
- ✓ Increase the useful life of the GAC
- ✓ Reduce treatment costs for GAC regeneration; energy, water and air treatment


ADSORPTION
Effluent
Recirculation Loop
GAC
Trap
Fe amended
GAC
Mixing
Reservoir
Influent
Pump


OXIDATION
Effluent
Recirculation Loop
GAC
Trap
Mixing
Reservoir
Influent
Pump

ADSORPTION / REGENERATED CARBON



Hydrogen Peroxide (H_2O_2)

- pH
  - Conventional wisdom in soil systems (revised)
  - Recent studies suggest pH plays minor role in the regeneration of MTBE-spent GAC
- H_2O_2 concentration (increase)
  - Rate and extent of oxidation increases
    - source term for •OH: $k_1 [H_2O_2] [Fe^{+2}]$
  - Oxidation efficiency decreases (H_2O_2 scavenging)

    $H_2O_2 + \bullet OH \Rightarrow \bullet HO_2 + H_2O$
  - Optimal [H_2O_2] – treatment objective: (1) time, rate of regeneration; (2) cost

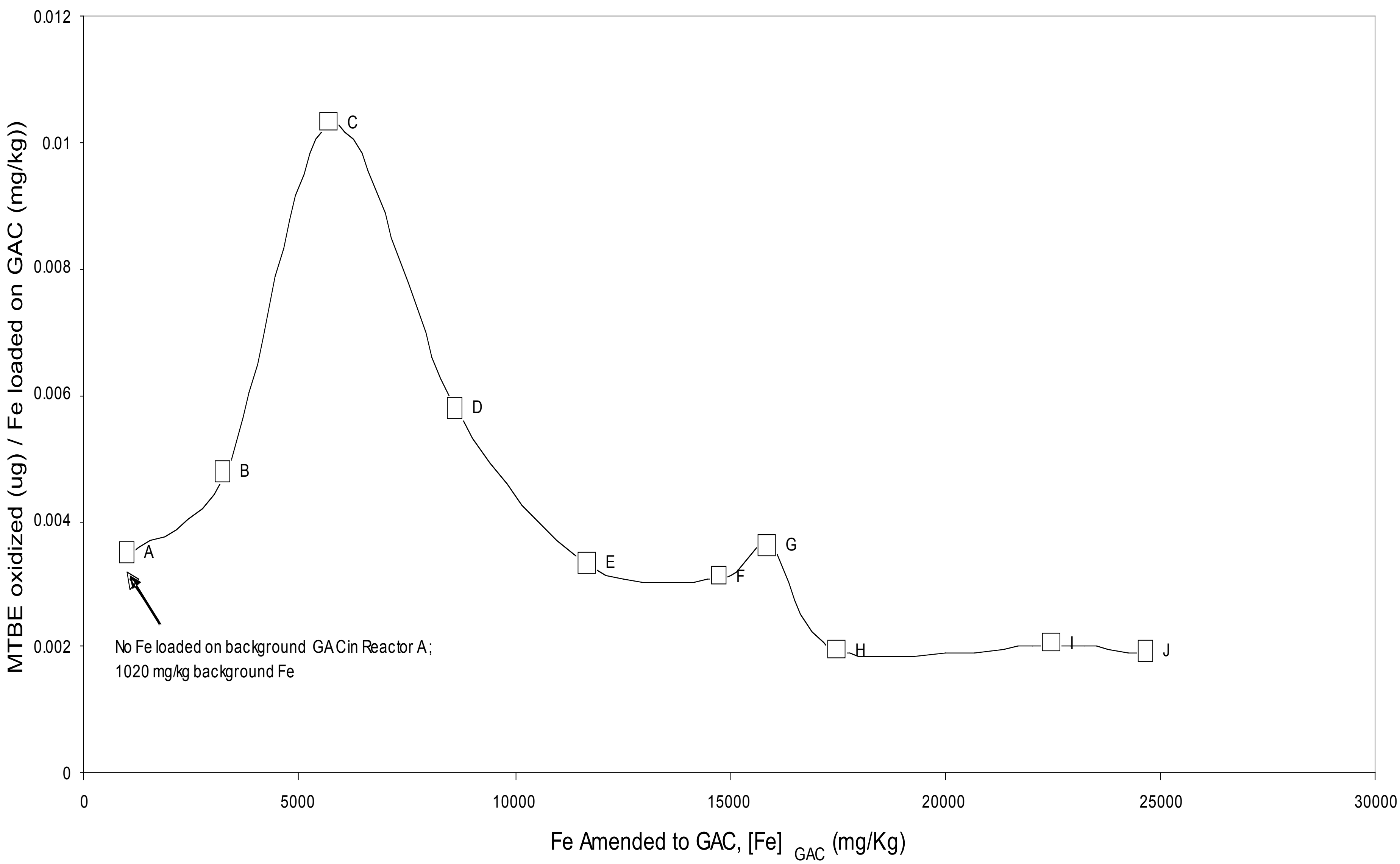
Iron (Fe)

- Fe amendment has enhanced GAC regeneration
- Iron solutions amended to GAC are acidic
  - Generally good (BSO reduction, ASO production)
- Counter-ion of ferric iron
  - Cl^-, SO_4^{2-}, NO_3^-
- Blockage of the pore structure by Fe oxides
  - Complexation, precipitation, ion exchange
  - Freshly added - predominantly poorly ordered, amorphous
  - Small effect on surface area and PVD by moderate increases in Fe concentrations

Fe-amendment impact on surface area and pore volume distribution (Huling *et al.*, 2005a).

	[Fe] (mg/kg)	BET Surface Area (m^2/g)	Pore Volume Distribution Micro-	Meso+Macro (ml/g)	Total
Fe-unamended	1380	1385	0.536	0.193	0.728
Fe-amended	10360	1303	0.512	0.175	0.687
	(n=4)	(n=9)		(n=9)	

Maximum Fe loading oxidation efficiency



Physicochemical Effects: Adsorbate-free

- Repeated H_2O_2 treatments in Fe-amended, adsorbate-free GAC (Huling *et al.*, 2005a)
  - H_2O_2 applied in 15 sequential applications (pH 3.5)
  - No adsorbate was present during the oxidation (oxidative effects vs adsorbate/decomposition products)
  - 4 % loss in GAC
  - 15% loss in surface area
  - 30% reduction in Iodine number
  - 37% loss in micropore volume
  - Increase in the meso+macro pore volume
  - Loss in sorption capacity for 2CP, TCE, MTBE

Physicochemical Effects:
MTBE Amended

- Multiple regenerations using repeated H_2O_2 treatments in Fe-amended, MTBE-spent GAC (Huling *et al.*, 2005b)
  - Two full regeneration cycles (adsorption/oxidation 2X + adsorption).
  - Transformation of MTBE, TBA, and acetone.
  - 91% GAC regeneration.
  - Approximately 5X less loss in surface area and pore volume was measured; no loss in sorption capacity for MTBE.
  - GAC protected by adsorbate/byproducts.
  - Optimal balance – strength/number oxidative treatments vs. anticipated effects on the sorptive characteristics of GAC.

GAC Regeneration

- ✓ Wide range of environmental contaminants
  - ✓ adsorption + oxidation (reduction)
- ✓ Chemicals tested
  - ✓ TCE 73–95% (De Las Casas *et al.*, 2005)
  - ✓ MC 100% (De Las Casas *et al.*, 2005)
  - ✓ CF 94% (De Las Casas *et al.*, 2005)
  - ✓ NDMA >99% (Kommineni *et al.*, 2003)
  - ✓ MTBE 91% (Huling *et al.*, 2005b)
  - ✓ DIMP 97-98% (Huling and Jones, 1999)

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SUMMARY

- AC - BEST AVAILABLE ADSORBENT
- COMMERCIAL AC's VARY CONSIDERABLY IN PERFORMANCE
- PERFORMANCE IS RELATED TO RAW MATERIAL SOURCE AND MANUFACTURING CONDITIONS
- THERMAL REGENERATION: OFF-SITE, HIGH TEMP ,WEIGHT LOSSES (~15%), CHANGES PSD, PVD
- FENTON REGENERATION:ON-SITE, AMBIENT TEMP., WEIGHT LOSSES(<1%), MIN. PSD, PVD CHANGES

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THANK YOU