PLASMACHEMISTRY

- **40 % of technology steps in the microprocessor manufacturing**
- **Production of ozone and other gaseous products**
- **surface modification of materials:** *surface nanotechnology of polymers, superhard materials, clean technology*
- **cleaning technology**– *destruction of toxic materials*
- **Plasma medicine and plasma agriculture**
- **Excimer lasers and lamps**

• Thermal (equilibrium) plasmas:

The whole gas is heated in order to make the desirable chemical changes and all plasma components (molecules, ions, electrons) have the same temperature on the order of 1 eV (1 eV = 1.6×10^{-19} J, and corresponds to 1.16×10^{4} K).

Saha ionization equation is an expression that relates the ionization state of a gas in thermal equilibrium to the temperature and pressure. It can be derived from Boltzman equation.

Thermal (equilibrium) plasmas:

are usually generated using **DC or RF plasma furnaces or torches,** where a plasma gas is heated in order to make the desirable chemical changes.

Thermal plasma technology offers several **processing benefits** when compared to more conventional thermal treatment processes:

- the availability of high temperatures;
- flexibility in operating in either reducing or oxidizing environments
- low gas requirements
- the ability to treat a large variety of waste streams

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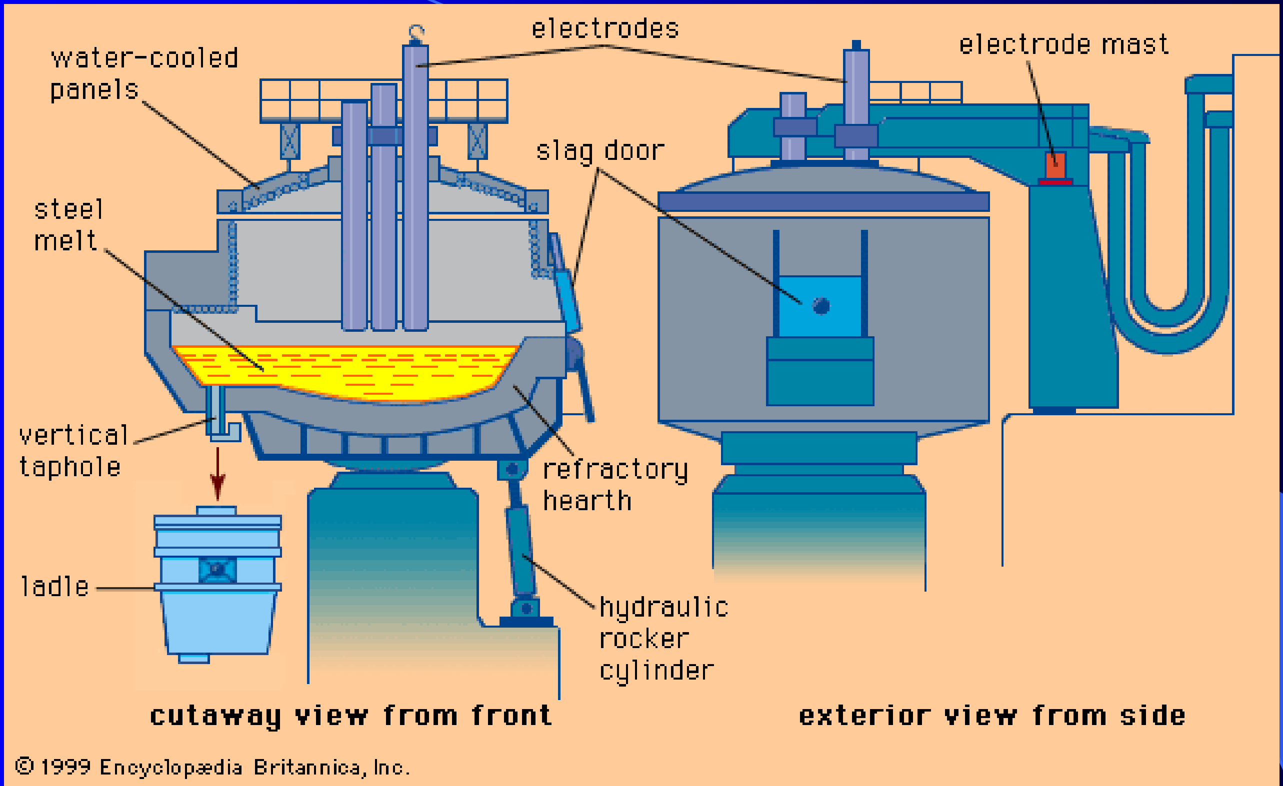
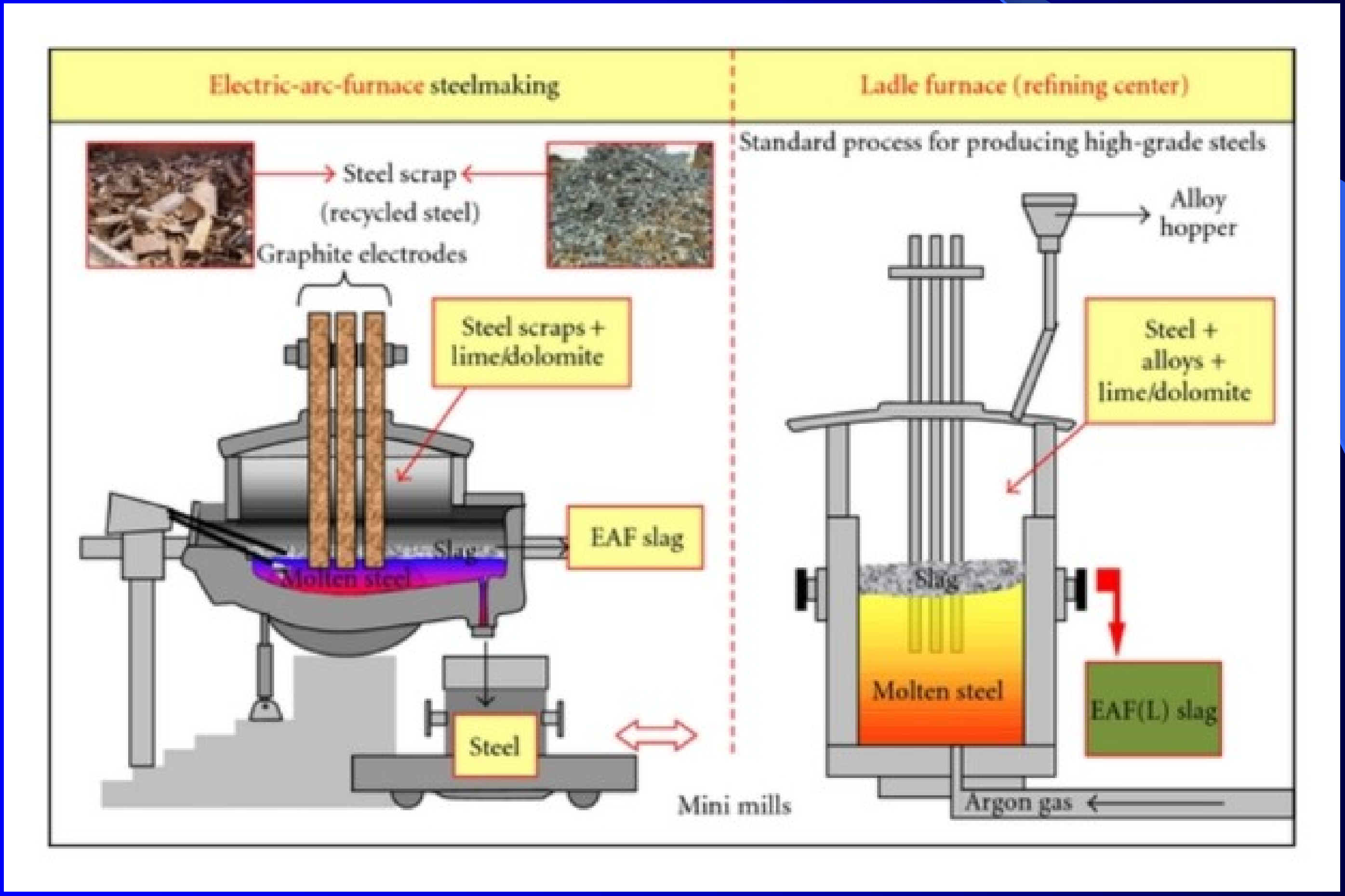
DC Electric Arc Furnace Steelmaking



An electric arc is formed between the electrodes and the metallic charge and charge is heated from the arc radiation. The DC arc current flows from **carbon cathodes**, which acts as cathodes, to an anode embedded in the bottom of the furnace.

DC Electric Arc Furnace Steelmaking

A mid-sized modern steelmaking furnace would have a power of about 60,000,000 volt-amperes (60 MVA), with a voltage between 400 and 900 volts and a current in excess of 44,000 amperes.



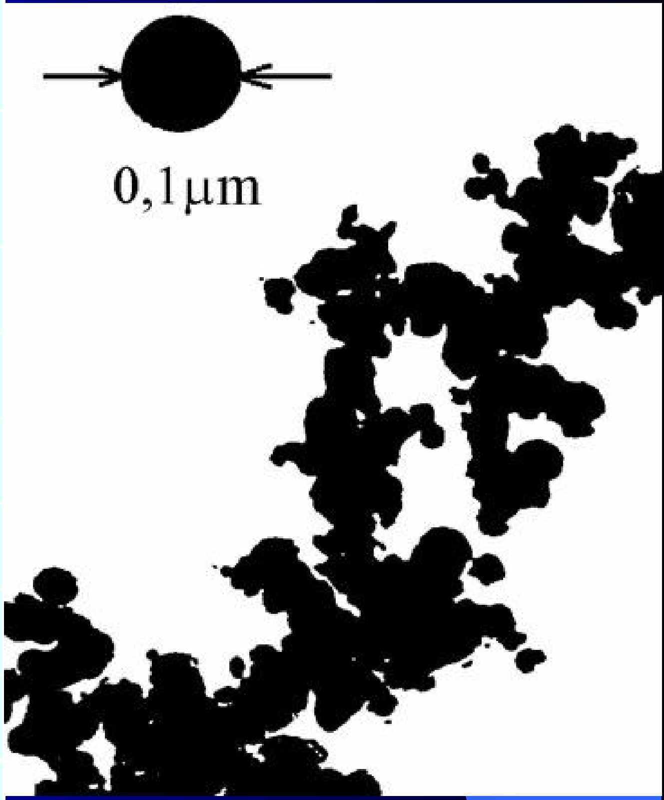
Refining operations in the electric arc furnace have traditionally involved the removal of phosphorus, sulfur, aluminum, silicon, manganese and carbon from the steel. In recent times, dissolved gases, especially hydrogen and nitrogen, been recognized as a concern. The refining reactions are all dependent on the availability of oxygen. **Oxygen was lanced at the end of meltdown to lower the bath carbon content to the desired level.** Most of the compounds which are to be removed during refining have a higher affinity for oxygen that the carbon. Thus the oxygen will preferentially react with these elements to form oxides which float out of the steel and into the slag.

Manufacturing of nano-powders powders

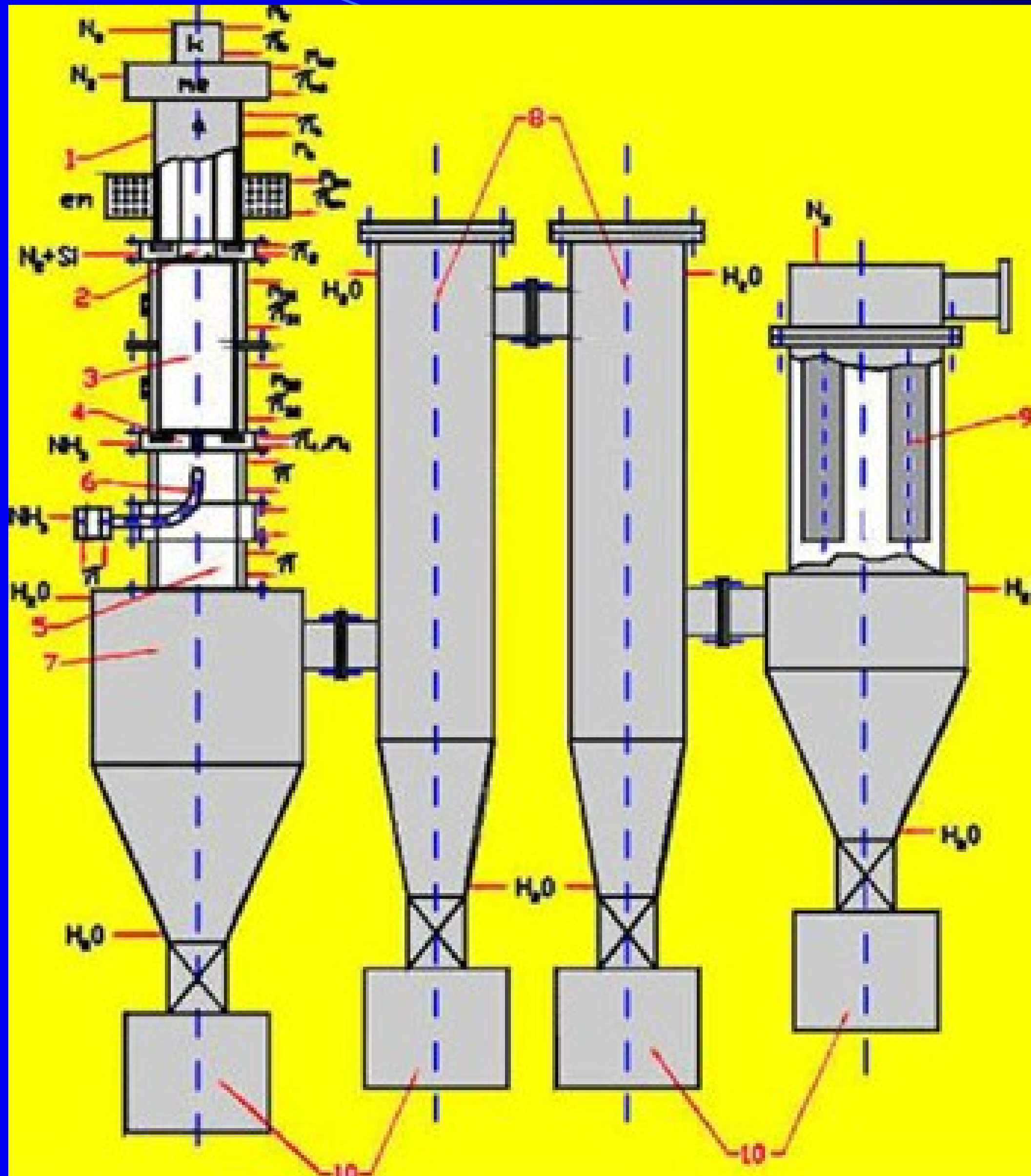
Characteristics of the nano-phase ceramic powder synthesized in thermal plasma

. Silicon nitride Si_3N_4

Raw material	Si powder +N_2+NH_3
Color	Grey-white
Specific surface (BET method)	40-100 m^2/g
Equivalent particle diameter	20-50 nm
Nitrogen content	35-38%
Free Si content	< 1%
a-Si_3N_4 content	15-30%
b-Si_3N_4 content	5-10%
Amorphous Si_3N_4	50-65%

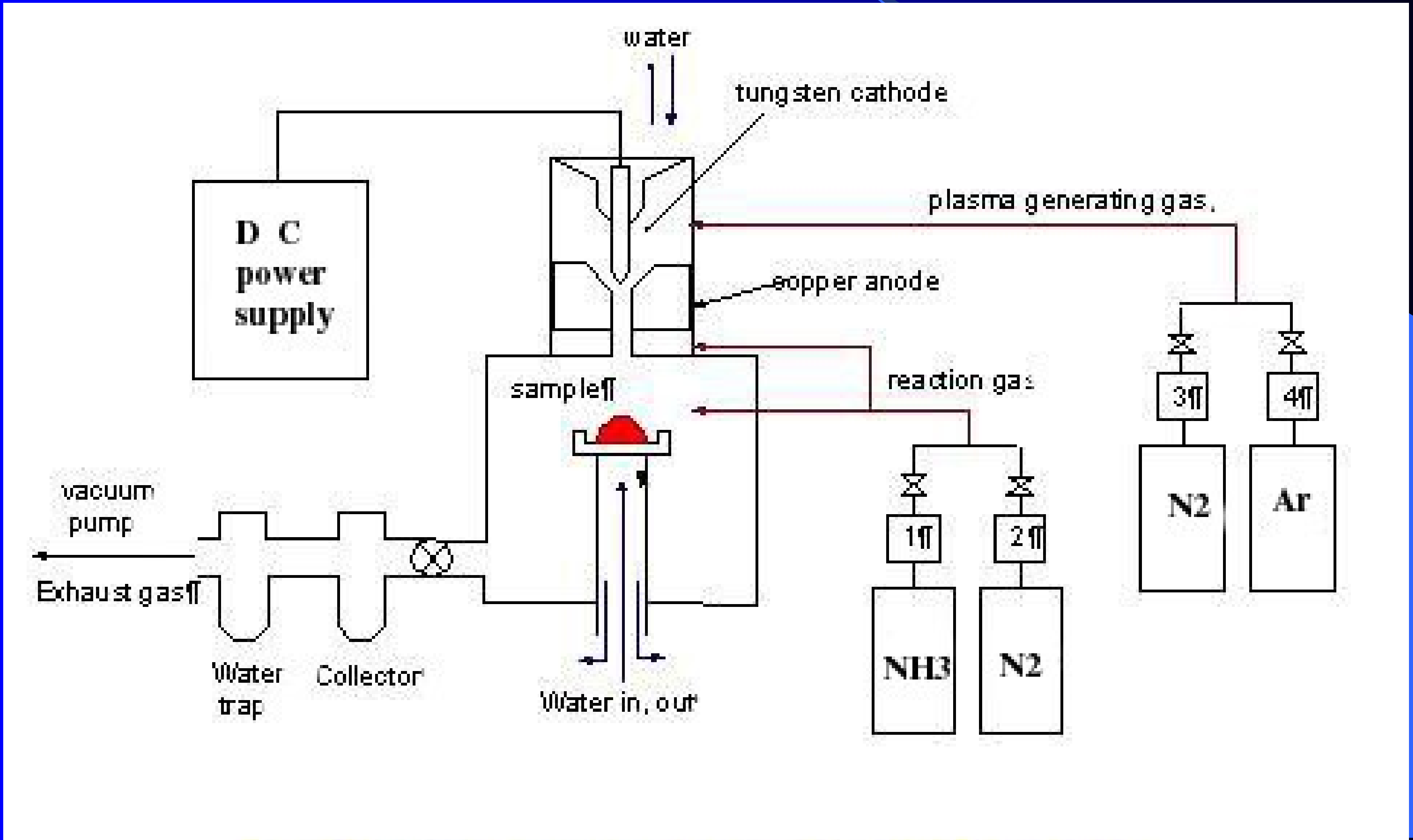


Inductively coupled RF *thermal plasma* source



Manufacturing of nano-powders powders

DC plasma apparatus for AlN nanopowder generation



Thermal plasmas can be generated by various means – direct current (DC) arcs or radio-frequency (RF) arcs. Typical thermal plasma temperatures are in the range **10,000 K to 30,000 K** and result in heat transfer rates (enthalpy !) that are difficult to match by alternative processing techniques.The plasma arc torch uses metallic or carbon electrodes to create an arc. The plasma torch and electrodes are water-cooled and the average life of the electrodes ranges between o**200 to 500 hours** f operation. A DC power supply unit provides the electrical requirements of the torch and commercial units are available in power levels ranging from about 100 KW to 10 MW capacity. The process is about 90 percent efficient in energy usage.

Conversion of methane to acetylene in isothermal plasma

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

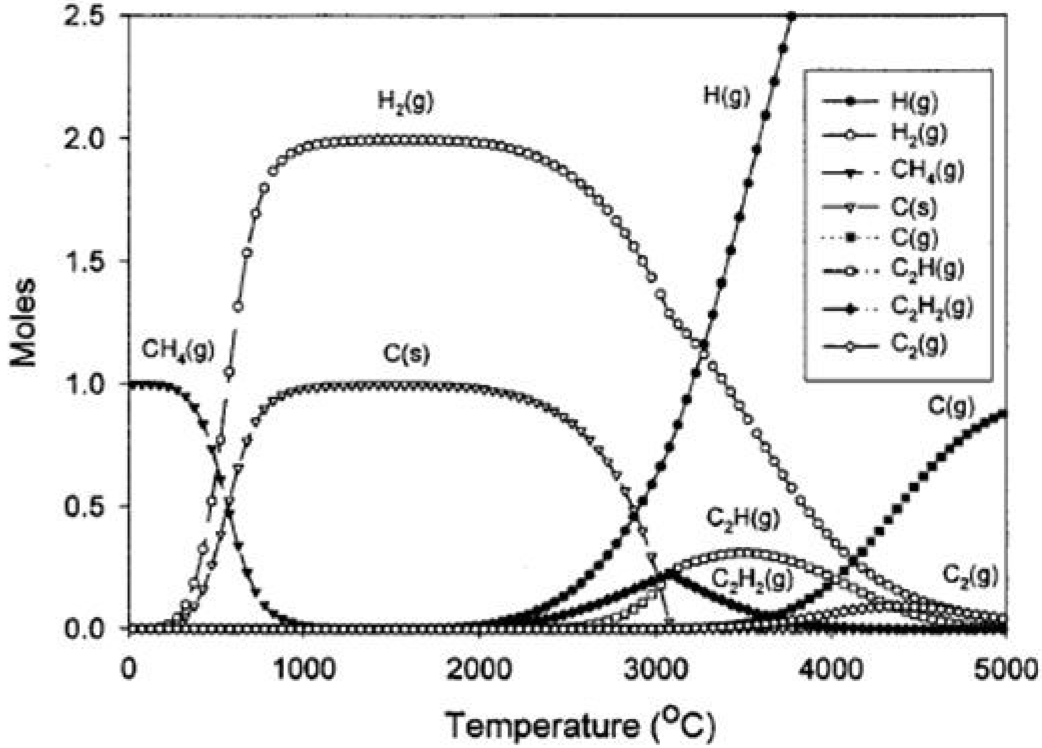
The Huels process has been in commercial use in Germany from 1938. The electric Arc reactor of Huels transfers electrical energy by direct contact between the high temperature arc (15,000 – 20,000 K) and the methane feed stock. **The product gas is quenched with water and liquefied propane to prevent the back reactions.**

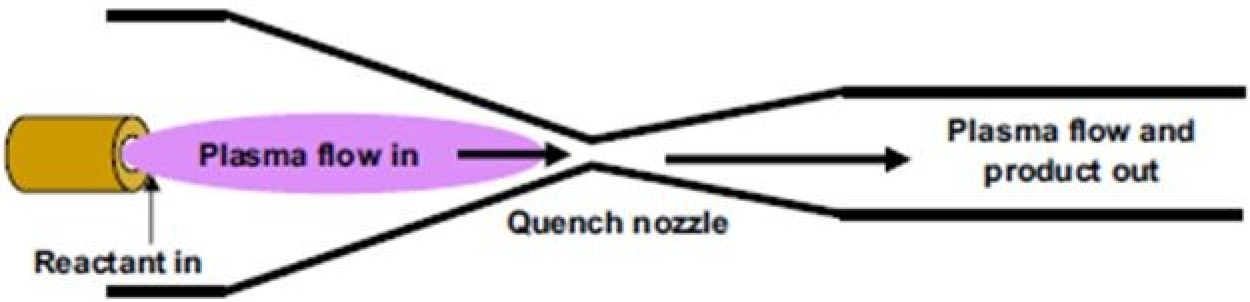
Single pass yield of acetylene is less than 40% and the overall yield of acetylene greater than 60% by recycling all the hydrocarbons except acetylene and ethylene

The Huels process produces a significant amount of carbon deposit on the electrodes, which requires periodic shut down of the conversion process and performs a steam reforming cleaning of the electrodes. **Although in commercial use, the Huels process is only marginally economical.**

A challenge for non-equlibrium plasma applications !!!

Utilized Technology : Huels Process (CH_4 ➡ C_2H_2)

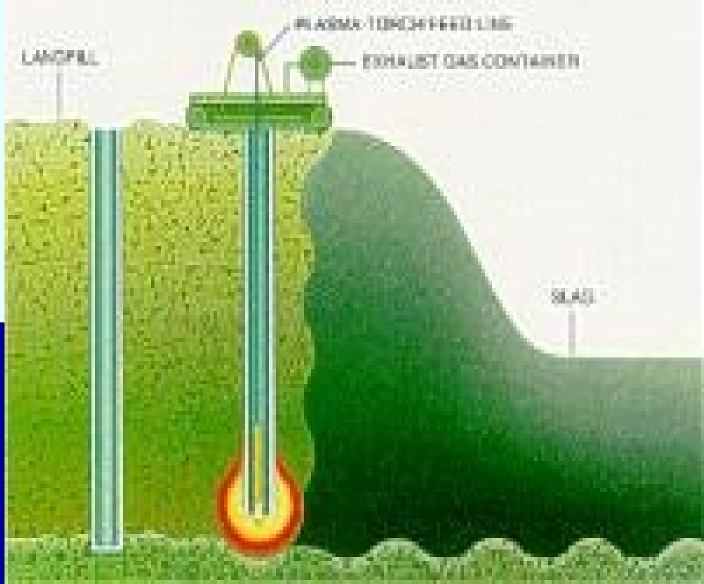




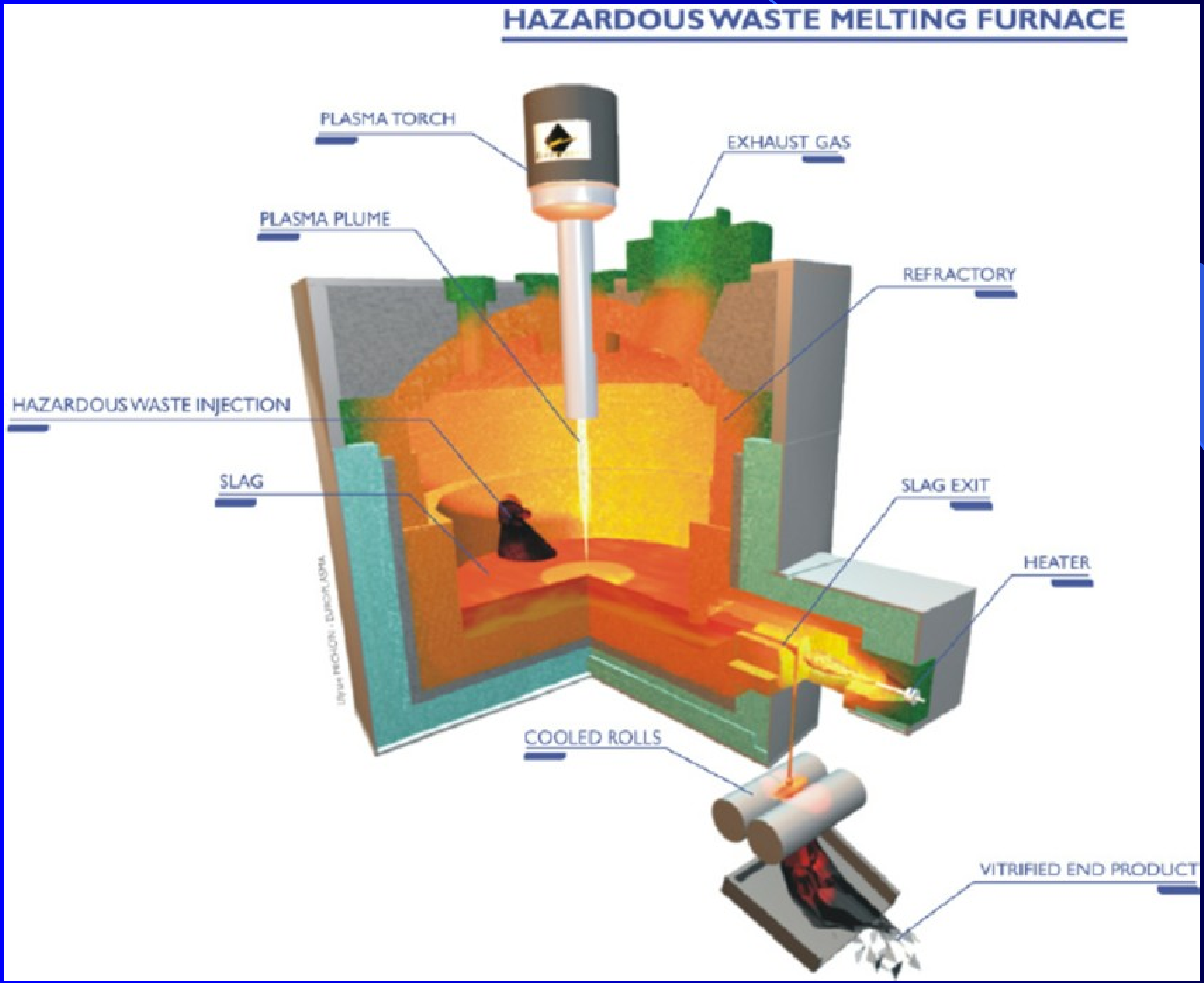
Report from
Idaho Nat'l Lab (2007)

Thermal plasma for environmental waste remediaiton

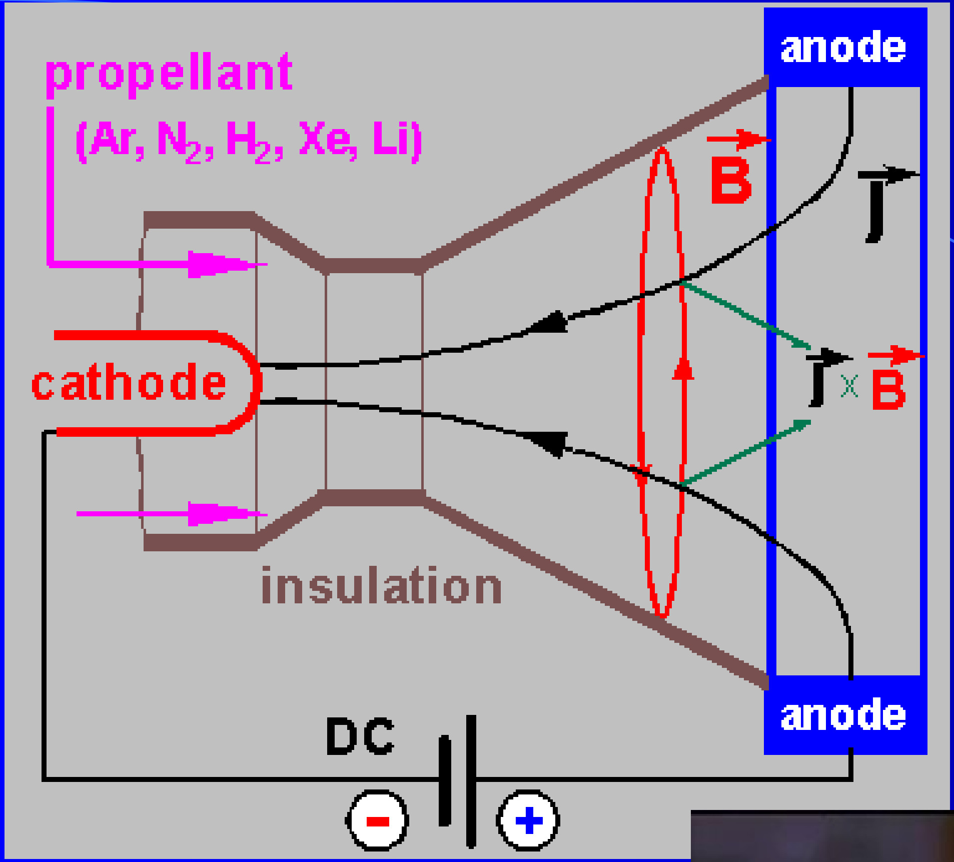
For many years, **in-situ thermal vitrification** has been recognized as one method to remediate contaminated soils and help stabilize land fills. However, the complexity of the process and the uncertainty of the results have limited the use of this remediation technique. Major technological advances in plasma arc technology now permit the in-situ transformation of all soil, rock, and waste types into vitrified, rock-like material, similar to obsidian, that is durable, strong, and highly resistant to leaching.

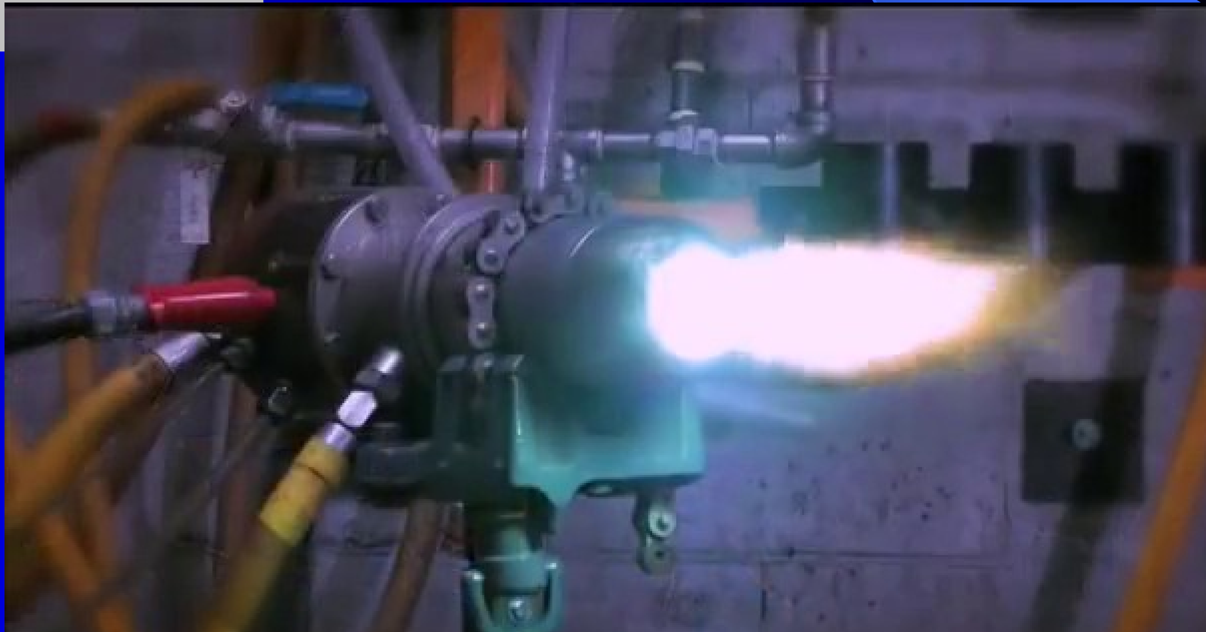


- Schematic of Europlasma reactor in CENON for fly ash vitrification with one 500 kW Aerospatiale plasma



DC plasma torch – minimizing of plasma gas flow by the effect of magnetic field

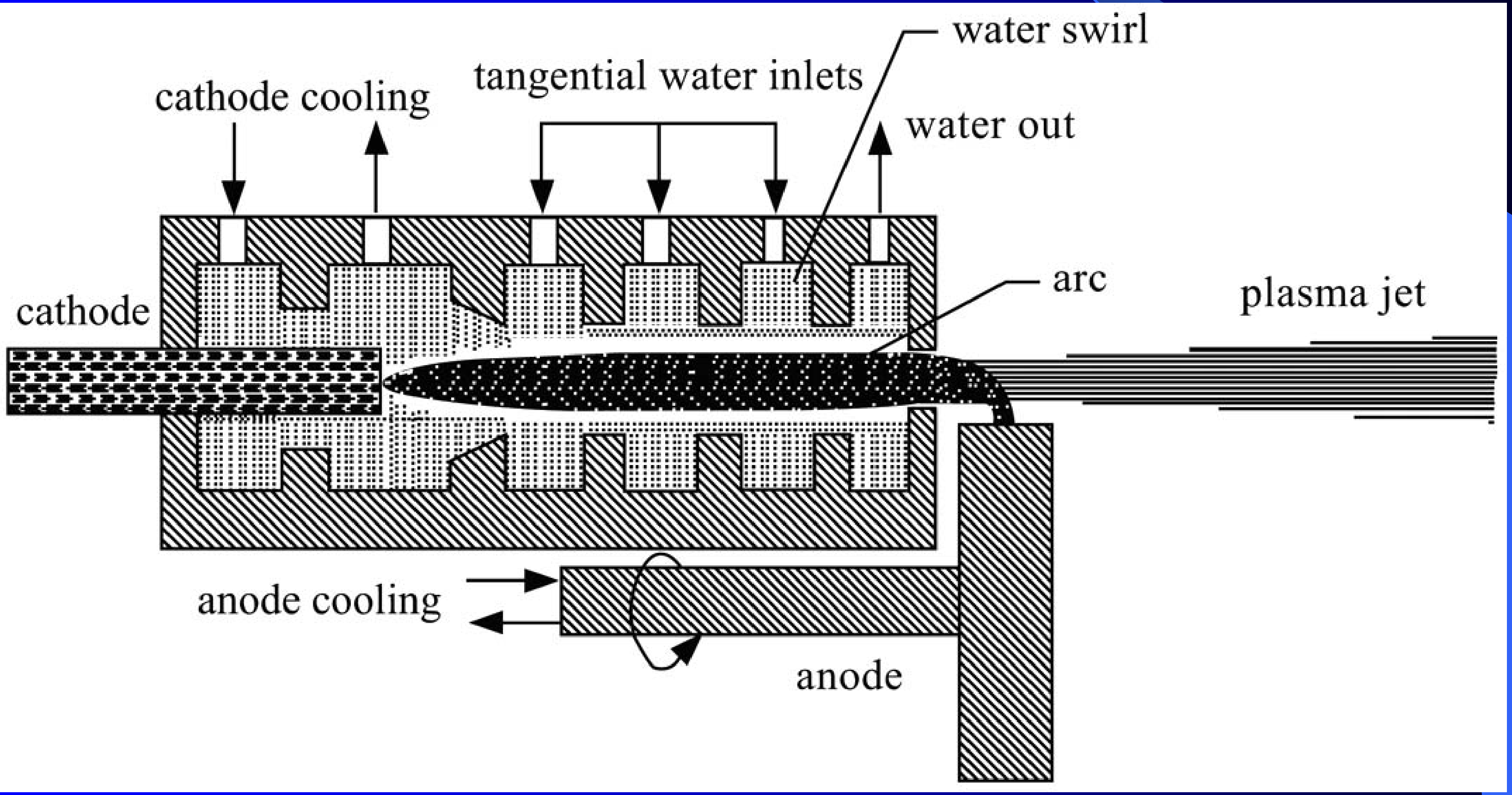




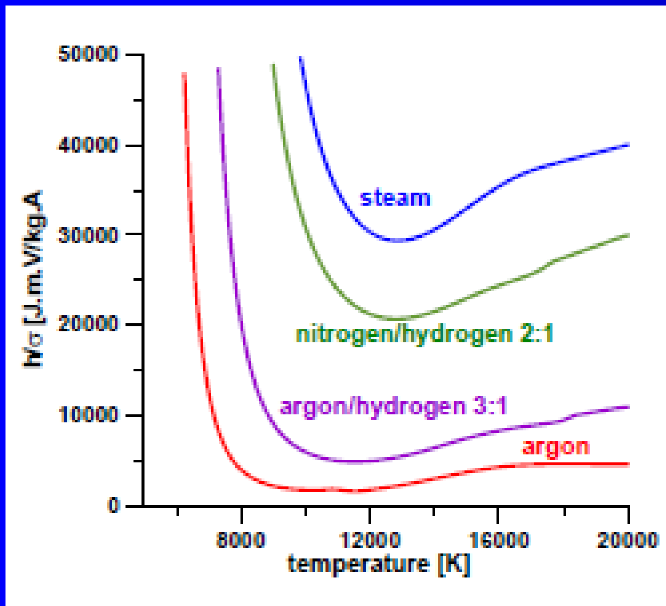
The thermal plasma gasification of biomass to produce synthesis gas (syngas) offers an alternative to fossil fuels. Since syngas contains hydrogen and carbon monoxide, it has the potential to be used as a re-burning fuel to reduce NOx emissions. Common biomass gasification technologies are based on the reaction between a heated carbon source with limited amounts of oxygen and steam. Thermal plasma offers possibility of decomposition of biomass by pure pyrolysis in the absence of oxygen. In the process all energy needed for gasification comes from plasma, no energy for decomposition is produced by combustion. The process acts also as energy storage – electrical energy is transferred to plasma energy and then stored in produced syngas. The main advantage is better control of composition of produced gas, higher heat capacity of the gas and reduction of unwanted contaminants like tar, CO2 and higher hydrocarbons.

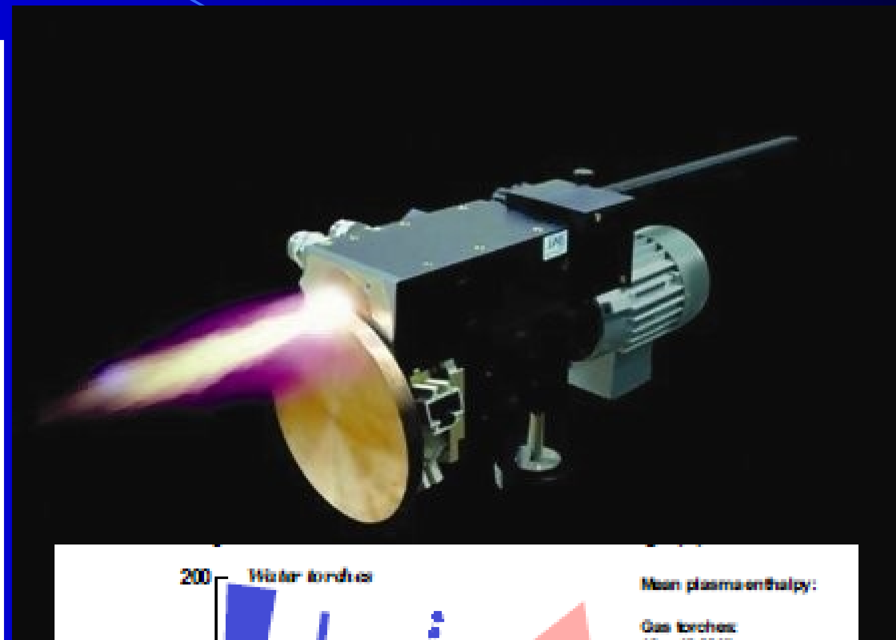
Thermal Plasma Generators with Water Stabilized Arc

Inst. Of Plasmaphysics, Prague



High – enthalpy of water plasma





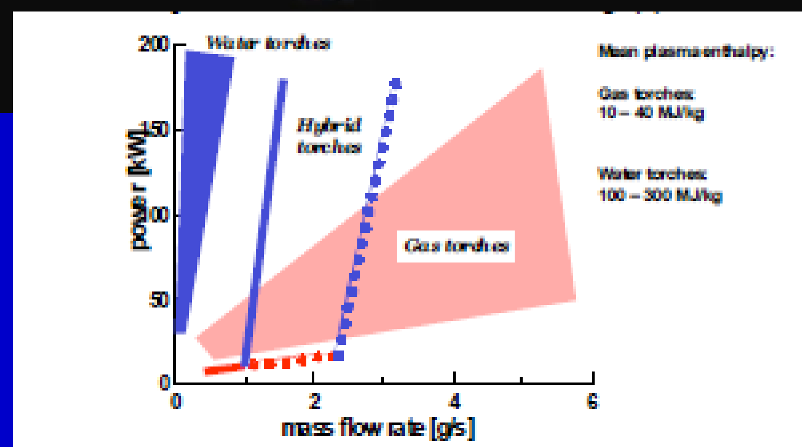


Fig. (8). Operation regimes of dc arc plasma torches.

Non-thermal (non-equilibrium) plasmas

- The electron mean energies are considerably higher than those of the components of the ambient gas. The majority of the electrical energy goes into the production of energetic electrons rather than into gas heating. The energy in the plasma is thus directed preferentially to the electron-impact excitation, dissociation and ionization of the background gas to produce radicals taking part in subsequent chemical reactions.

Electron energy dissipation in air:

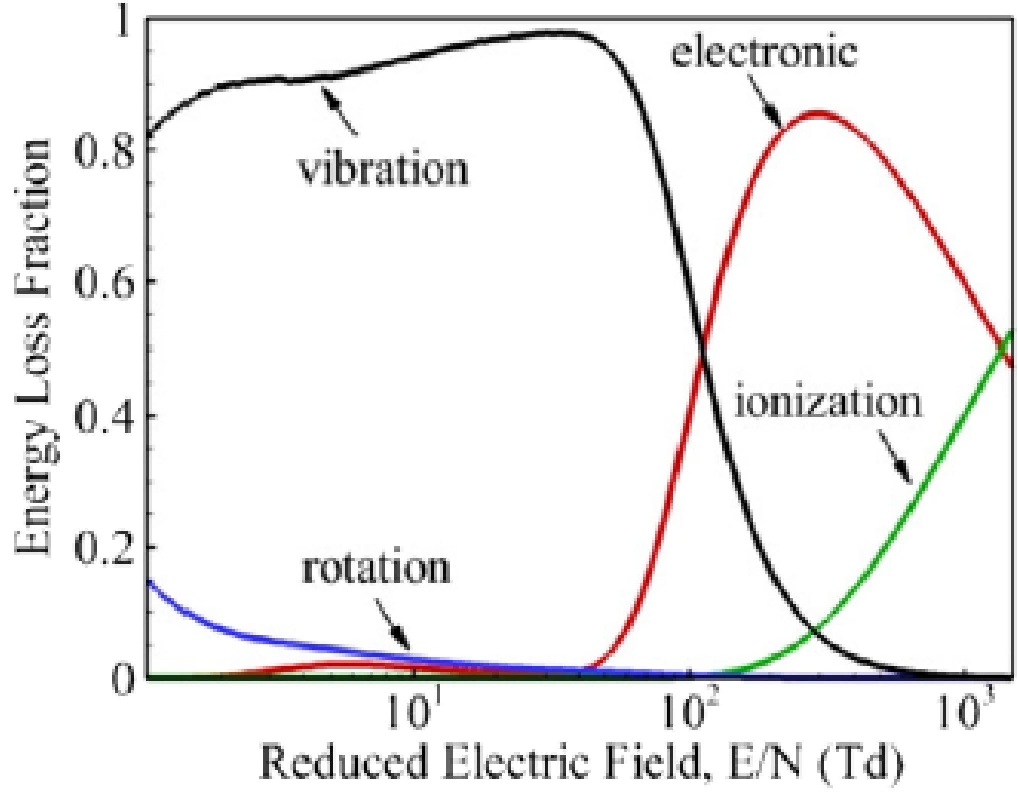
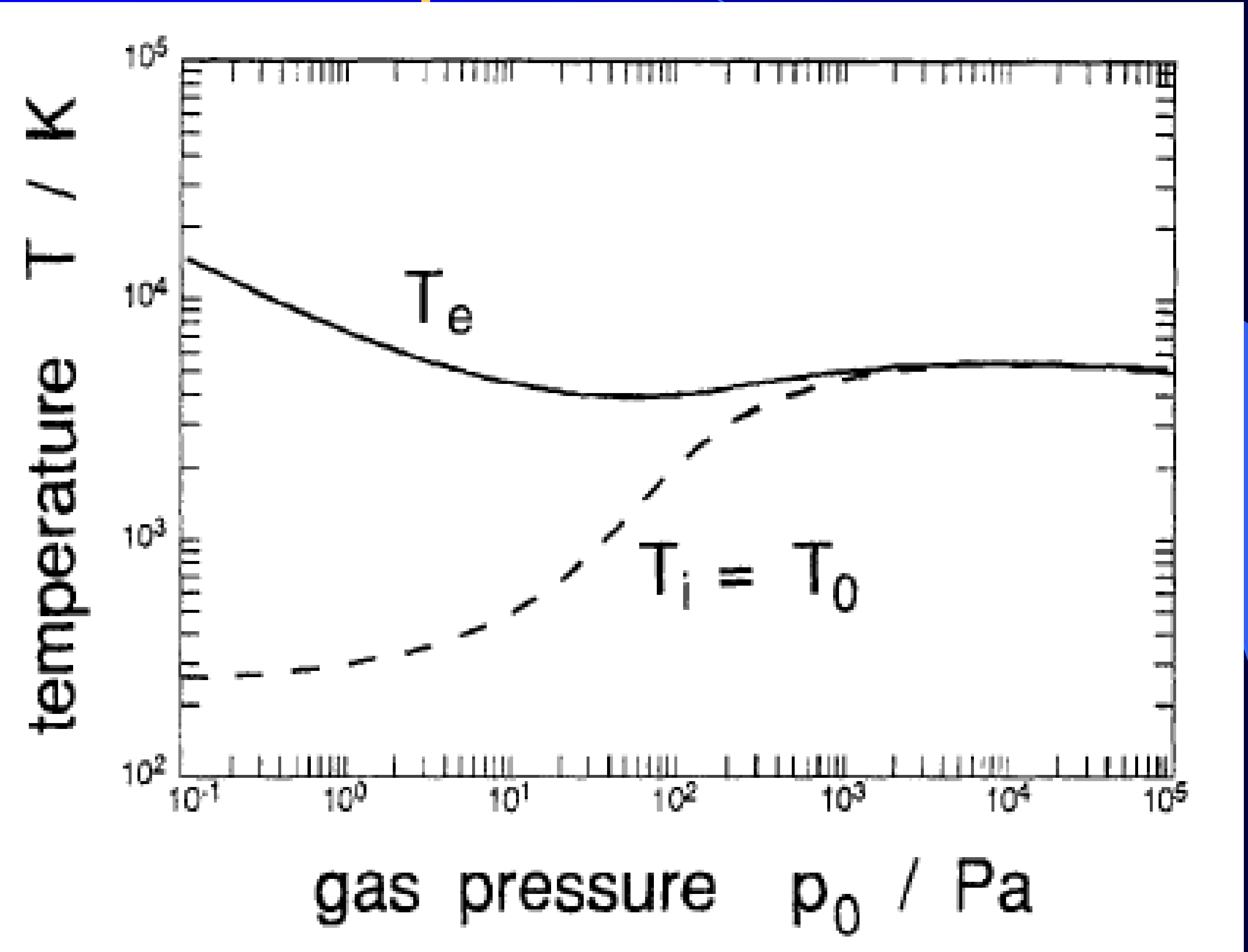


Figure 1. Fraction of electron energy lost in excitation of internal energy modes and ionization of O_2 and N_2 molecules in air as a function of reduced electric field, E/N.

Equllibrium and non-equllibrium plasmas



Electrical discharge plasmachemical processing

- ***Mean electron energy is on the order of 0.1 eV to 1 eV.***

Electrical discharges can be produced in many different forms, depending on the geometry of the reactor, electron power supply, operating gas pressure, etc. Sources which operate in vacuum are at a disadvantage with respect to those that operate at 1atm because of the increased capital cost and the requirement for batch processing of workpieces associated with vacuum systems. The development of atmospheric pressure plasma sources to replace plasma processing in vacuum system is a current trend in industrial plasma engineering.

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Electron beam processing:

- ***The electron energy is on the order of 100 keV to 1 MeV.***
- Conventional e-beam sources use thermoionic cathodes that are subject to poisoning and therefore require high vacuum near the cathode region. Plasma cathodes, which can operate at higher pressures, can be substituted for the e-beam sources, but have not been used in most applications because the emittance is usually not as good. The use of plasma cathodes, however, may significantly reduce the capital cost for implementing electron beam processing in plasmachemistry.
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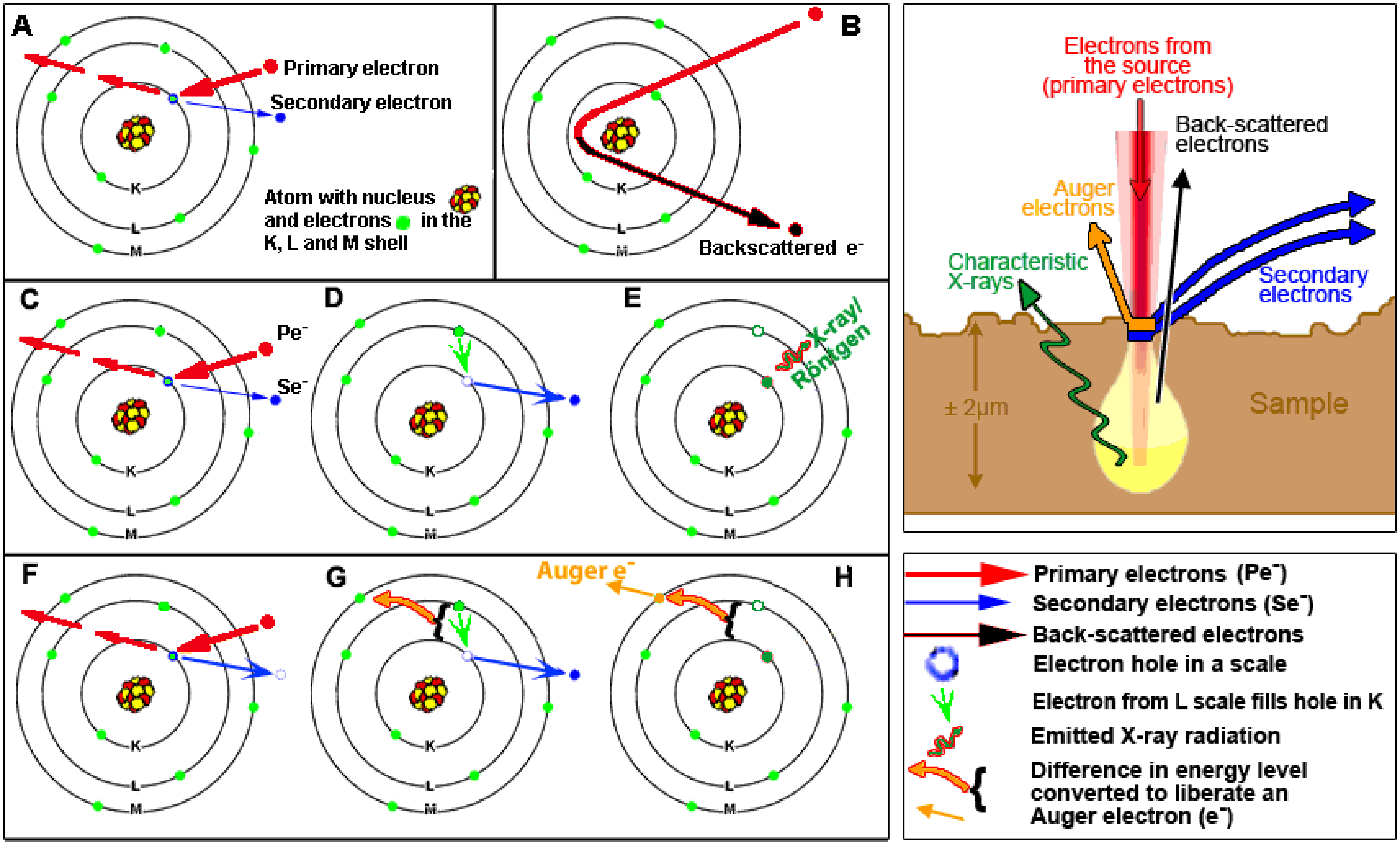
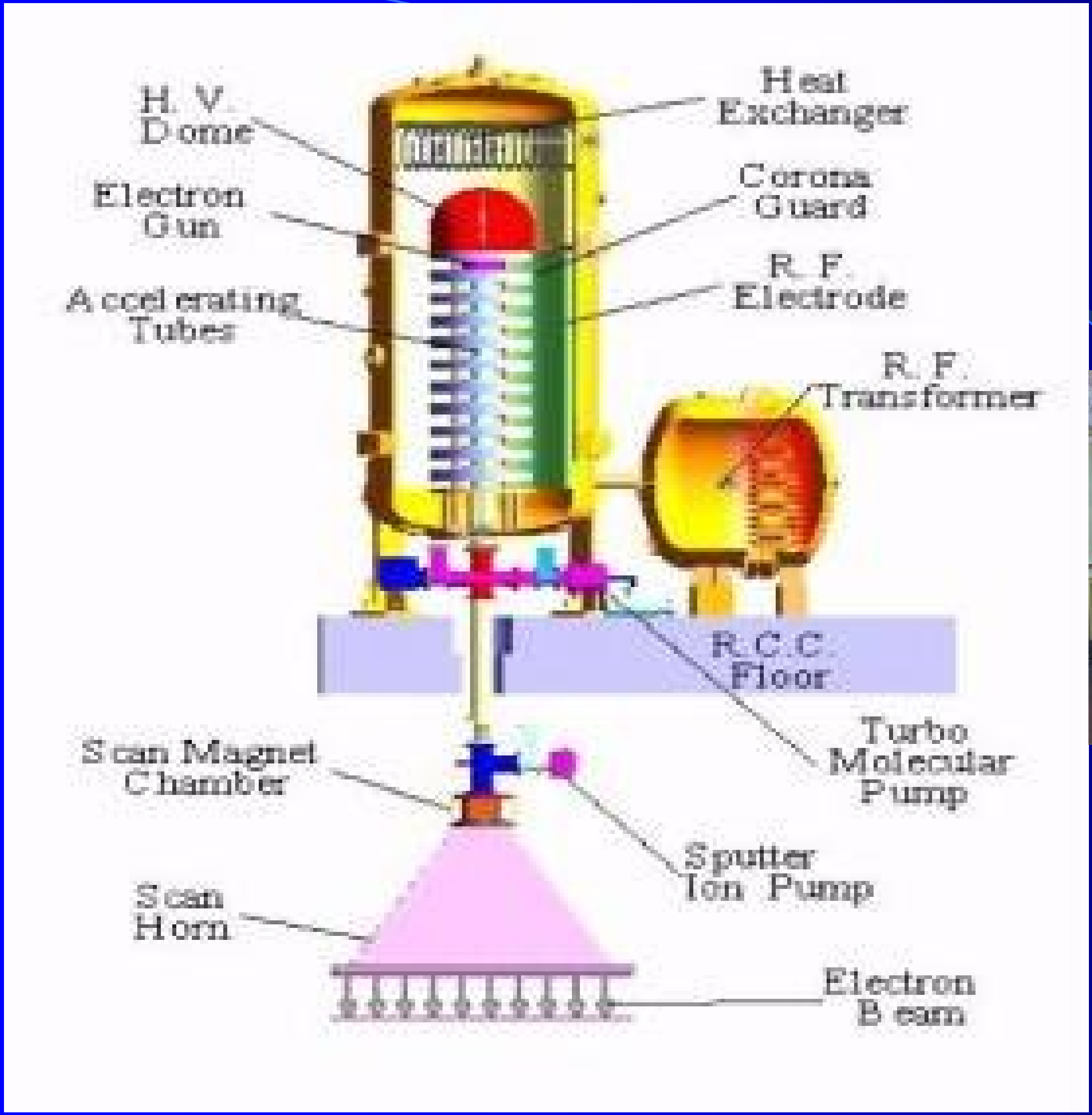
- **Fast electrons (100 keV to 1 MeV)** lose thier energy by inelastic collisions with electrons of target molecules forming secondary electrons and excited molecules. Secondary electrons are formed from fast primary electrons. The energy distribution of the secondary electrons has a maximum between 50 and 100 eV. Their penetration depth in solids and liquids reaches only few nanometers. Coulomb interaction of secondary electrons with valence electrons of neighboring molecules leads to the formation of radical cations, thermalized electrons, excited molecules and radicals. There are generated in “droplets” along the track of the fast electrons.



A
Primary electron
Secondary electron
Atom with nucleus and electrons in the K, L and M shell
K
L
M
B
Backscattered e-
C
Pe-
Se-
D
E
X-ray/ Röntgen
F
G
Auger e-
H
Electrons from the source (primary electrons)
Back-scattered electrons
Auger electrons
Characteristic X-rays
Secondary electrons
± 2µm
Sample
Primary electrons (Pe-)
Secondary electrons (Se-)
Back-scattered electrons
Electron hole in a scale
Electron from L scale fills hole in K
Emitted X-ray radiation
Difference in energy level converted to liberate an Auger electron (e-)

Polymer processing

The effects of the fast electrons on polymeric materials can be manifested in one of three ways: The polymer may undergo one or both of the two possible reactions: those that are molecular-weight increasing in nature, or molecular-weight reducing in nature. Or, in the case of radiation-resistant polymers, no significant change in molecular weight will be observed. The conventional term for irradiation-induced increase in molecular weight is cross-linking. The corresponding term for irradiation-induced decrease in molecular weight is chain scissioning (or degradation).


H. V.
Dome
Heat
Exchanger
Electron
Gun
Corona
Guard
R. F.
Electrode
Accelerating
Tubes
R. F.
Transformer
R.C.C.
Floor
Turbo
Molecular
Pump
Scan Magnet
Chamber
Sputter
Ion Pump
Scan
Horn
Electron
Beam

Electron beam sterilization