

中科院力学所  
CAS-IMECH

2014 Bioenergy and Biomass  
Utilization Summit, Shanghai

Ultra-Low PCDD/Fs Emission Gasification  
Technologies for Biomass and Wastes  
**超低二噁英排放的生物质和废弃物气化技术**

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LHD, I. Mech, CAS <http://www.imech.ac.cn>

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- Plasma Application in the World
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- High T Gasification
  - External Heat, 1000-1200 °C——PCDD/Fs and Tars



# Thermal Treatment Technologies

- ❖ Incineration—Very Popular in developed countries and many developing countries
  - Investment is huge, running cost is high
  - **May secondary pollution--dioxins**
  - MSW—Co-Gen:Stoker, Fluidized Bed, CFB
  - HW incineration—Rotary Kiln
  - MW—Small-sized incinerator
- ❖ Pyrolysis/gasification—H<sub>2</sub> and CO
- ❖ PP/V and PG/V—environment impact, biomass

# Dioxins

- ❖ PCDD/Fs : ITEQ-17 (Eadon-12, Nodic-17),
  - 75 PCDDs (PolyChlorinated Dibenzo-p-Dioxin, ITEQ-7)
  - 135 PCDFs (PolyChlorinated Dibenzofuran, ITEQ-10)
- ❖ WHO - 209 PCBs (Co-PCBs, ITEQ-12) -1998
- ❖ 850°C, 2s destroy, 250-500°C regeneration, /de novo



# 二噁英类毒性因子 (I-TEF for Dioxins)

PCDDs & PCDFs

Co-PCBs

WHO 1998

	Isomers	TEF
PCDDs	2,3,7,8-TeCDD	1
	1,2,3,7,8-PeCDD	1
	1,2,3,4,7,8-HxCDD	0.1
	1,2,3,6,7,8-HxCDD	0.1
	1,2,3,7,8,9-HxCDD	0.1
	1,2,3,4,6,7,8-HpCDD	0.01
	1,2,3,4,6,7,8,9-OCDD	0.0001
PCDFs	2,3,7,8-TeCDF	0.1
	1,2,3,7,8-PeCDF	0.05
	2,3,4,7,8-PeCDF	0.5
	1,2,3,4,7,8-HxCDF	0.1
	1,2,3,6,7,8-HxCDF	0.1
	1,2,3,7,8,9-HxCDF	0.1
	2,3,4,6,7,8-HxCDF	0.1
	1,2,3,4,6,7,8,-HpCDF	0.01
	1,2,3,4,7,8,9-HpCDF	0.01
	1,2,3,4,6,7,8,9-OCDF	0.0001

	Isomers	IUPAC No.	TEF
(Non-ortho)	3,4,4',5-TeCB	#81	0.0001
	3,3',4,4'-TeCB	#77	0.0001
	3,3',4,4',5-PeCB	#126	0.1
	3,3',4,4',5,5'-HxCB	#169	0.01
(Mono-ortho)	2',3,4,4',5-PeCB	#123	0.0001
	2,3',4,4',5-PeCB	#118	0.0001
	2,3,3',4,4'-PeCB	#105	0.0001
	2,3,4,4',5-PeCB	#114	0.0005
	2,3',4,4',5,5'-HxCB	#167	0.00001
	2,3,3',4,4',5-HxCB	#156	0.0005
	2,3,3',4,4',5-HxCB	#157	0.0005
	2,3,3',4,4',5,5'-HpCB	#189	0.0001

# PCDD/Fs control - Incineration

## ❖ In furnace: 3T + E

- **Temperature 1100°C**, Time, Turbulent, Excess air
- 10 kg PVC : < 0.1ng PCDD/Fs (>30m<sup>3</sup>)
- Inorganic Cl : little effect on Dioxins — De Novo

## ❖ Cooling process

- Regeneration : control Pentachlorophenol
- De Novo, <1% of Pentachlorophenol?
- Alkaline protection, no Oxygen
- Very low Cl:S ratio (Coal application)
- Reductive Condition !!!



# Plasma Technology for Waste

- ❖ MSW
- ❖ Hazardous Wastes
- ❖ POPs
- ❖ Chemical Weapon
- ❖ Biomass
- ❖ Low radiation waste
- ❖ PP/V and PG/V



## Advantages of PP/V

- ❖ Conventional Incineration
  - Lower T, 5-10 times Off-gas
  - Residues, Fly Ash – HW, Landfill
- ❖ Plasma Pyrolysis with Vitrification (PP/V)
  - Fast startup and shutdown
  - Higher T, Little Off-gas—Combustible
  - Harmless Byproducts: Glass Residue
    - (PP/V Plasma Pyrolysis with Vitrification)
  - For HW: High Efficiency/No Pollution



# Introduction to Plasma

- ❖ Plasma“**等离子体**” “电浆”，The 4th phase of substances
  - Ionized, and is neutral in macroscopically
- ❖ Hot plasma: 2000-30000° C-low T, over 30000-high T
- ❖ Cool plasma: low pressure, non balanced in thermodynamics
- ❖ 1950s, re-entry, Chinese space program
  - 1960s, NASA supported WPC to develop p
  - Metallurgy application, can control reaction
- ❖ Plasma technology
  - Torches-DC Mach-4.5 –Newest
  - Arc-DC or AC
  - High frequency – Chemical Engineering

等离子体炬型号  
MACH 3



型号	功率 (千瓦)	燃气流量		冷却水流量	
		(立方英尺/分)	(标立方/时)	(加仑/分)	(立方/小时)
<b>Marc3</b>	75-300	10-45	10-20	12-20	2
<b>Marc11</b>	300-2.5MW	30-250	50-400	80	15



## Electrical heating, more radicals

- ❖ Plasma  $T > 7000^{\circ}\text{C}$ , reaction  $T=1000-1600^{\circ}\text{C}$
- ❖ Rapid reaction
- ❖ Excellent environmental impact, energy saving and near zero PCDD/Fs emission
  - POPs, Chlorines destroys radicals during combustion
  - Less off gas, easy to clean, valuables, liquid fuels
  - Vitrified slag,
  - Gas engine or gas turbine to generate electricity

# Plasma waste treatment

## ❖ More than 20 years

- 1970s, low radiation waste, CW
- 1990, WPC, 100 wastes, MSW
- Now, HW, PCBs, fly ash, etc.

## ❖ Alternative to incineration—high level industry

- MSW
- HW and POPs – Low cost
- Biomass to power
- Dioxin emission excellent



**250 kW 直流炬**

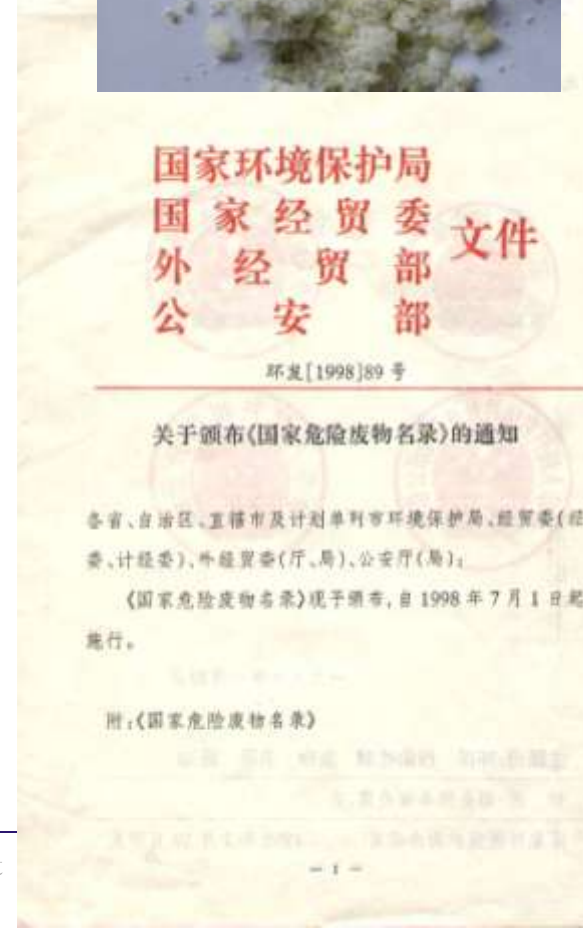


# Clean off-gas for Plasma Gasification

Pollutents	Unit	Plasma	GB18484 -2001	GB18485 -2001	Euro92	Euro2000
PCDD/Fs	ng/Nm <sup>3</sup> (TEQ)	<b>~0.0001</b>	0.5	1.0 (0.1)	0.1	0.1
Dust	mg/Nm <sup>3</sup>	0.38~0.69	65~100	80	30	10
CO	mg/Nm <sup>3</sup>	1.25~1.75	80~100	150	150 (Hr)	50 (Day)
NO <sub>x</sub>	mg/Nm <sup>3</sup>	0.03~0.05	500	400	400	200 (400)
SO <sub>2</sub>	mg/Nm <sup>3</sup>	0.29~0.38	200~400	260	260	50
HCL	mg/Nm <sup>3</sup>	2.00~5.00	60~100	75	50	10

# Hazardous waste treatment

- ❖ HW name list – 47 kinds of HW
  - HW01 Medical W
  - Based on BASEL CONVENTION
- ❖ 《中华人民共和国监控化学品管理条例》
  - 可作为化学武器；
  - 可作为生产化学武器前体；
  - 可作为生产化学武器主要原料；
  - 除炸药和纯碳氢化合物外的特定有机化学品
- ❖ CW destruction—2nd WW
- ❖ Chemical plant byproducts
- ❖ POPs—Stockholm Convention





# Plasma Application in the World

- ❖ MSW—WPC, Plasco Energy-94 t/d, EER-12t/d
  - WPC - AlterNRG, Geoplasma, Tees Valley - AP G65 X 2, Shanghai-GTS 50 tones, Bijie – GES G65 X 2 600 tones/d
- ❖ Industrial—InEnTec-PEM, PEAT, StarTec,
- ❖ HW/MW: WPC-India X 2
- ❖ POPs—Australian gas/liquid, Cas-Imech X 2
- ❖ CW—Monster II
- ❖ Biomass
- ❖ Low radiation waste

# Westinghouse Plasma Corp., Alter NRG

## ❖ 6 commercialized sites

- Mihama Mikata, 20t/d+4t/d sewage slurry, 2002
- Utahinai, 220t/d, 2003
- Madison, WPC & Alter NRG, Coskata Alcohol, 2003
- Pune, 68t/d, chemical waste, 2008
- Nagpur, 68t/d, chemical waste, 2008



## ❖ Gunma, 151t/d, 2000

## ❖ Madison, 1990, 48t/d

- Waltz Mill Site







# Application — WPC

## ❖ G65—1000 t/d

- Oxygen-700t/d MSW (2500-3000t Beijing) + 5 t Medical Waste+20 t waste tires+275t Coal, Air - 500t/d MSW, H=20.2m, D=9.7m, 65000 Nm<sup>3</sup>/h
- Marc - 4.5 (800kW) X 6, 25 MWe, 162t/d Diesel Fuel
- Investment RMB 1.1 B, Cash > RMB 400 M
- Air Products, Tees Valley G65 X 2
- Green Energy Solutions, BiJle G65 X 2, 600t/d
- Geoplasma — St. Lucie, 540 t/d - 2008.11
- Green Power—Tallahassee, 910t/d, 35MW, 2008.06

## ❖ WuHan Kedi — wood dust 50t/d



Westinghouse Plasma Corporation

*a division of Alter NRG Corp.*

提斯谷项目的附属模块  
的工程和建造在最后收  
尾阶段



# GTS示范项目

## Medical Waste + Fly Ash

Alter NRG为正在建设中的上海示范项目交付了气化炉设计和等离子炬，预计将于2013年第三季度进行调试。

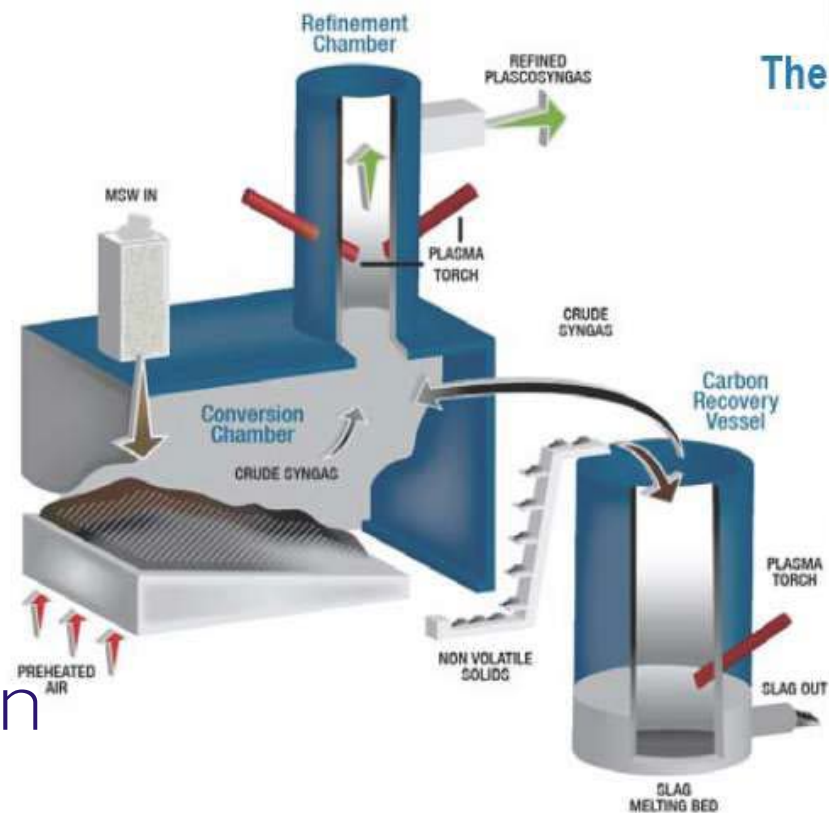
该设施将处理相混合的医疗废物和焚烧炉飞灰，主要是高效地集中处置医疗废物和其潜在的环境危害和公共卫生风险。由于焚烧炉飞灰是在中国日益增加的处置问题，它已成为中国政府的高度关注的的环境问题。

正在兴建的GTS设施，位于上海城投（上海环境）在嘉定区的现有危险废物处理设施。该设施将整合现有的焚烧炉来处理医疗废物，焚烧飞灰和其难处理的危险废物。该工艺设施将用于生产蒸汽。该集成系统是灵活的，会对废物控制采取综合处理和处置方法，如重复使用，回收，消毒和填埋，以尽量减少废物对环境健康的影响。



## Plasco Energy, CAN

- ❖ Ottawa 94 tons/d
- ❖ 5-GE gas engines
  - NOx and organics problems
  - 150 million CAN Dollars
- ❖ Ottawa – not applied
  - 400 tons/d
  - Tipping Fee 10 million Dollars
- ❖ Beijing 100t/dX2, not going on
- ❖ China Energy Saving Group



The h

# Plasco Energy Demo



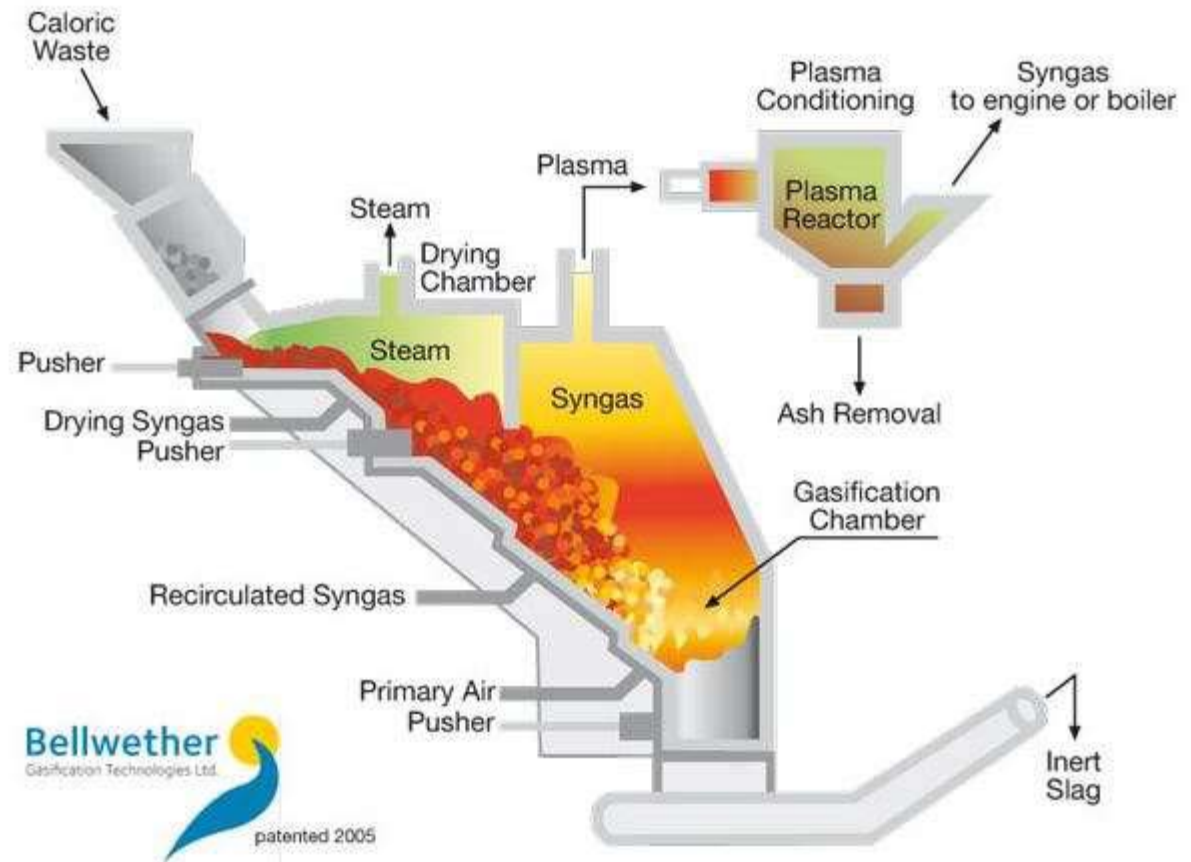
# Bellwether Gasification Technologies Ltd.

- Germany
- IMG Tech.

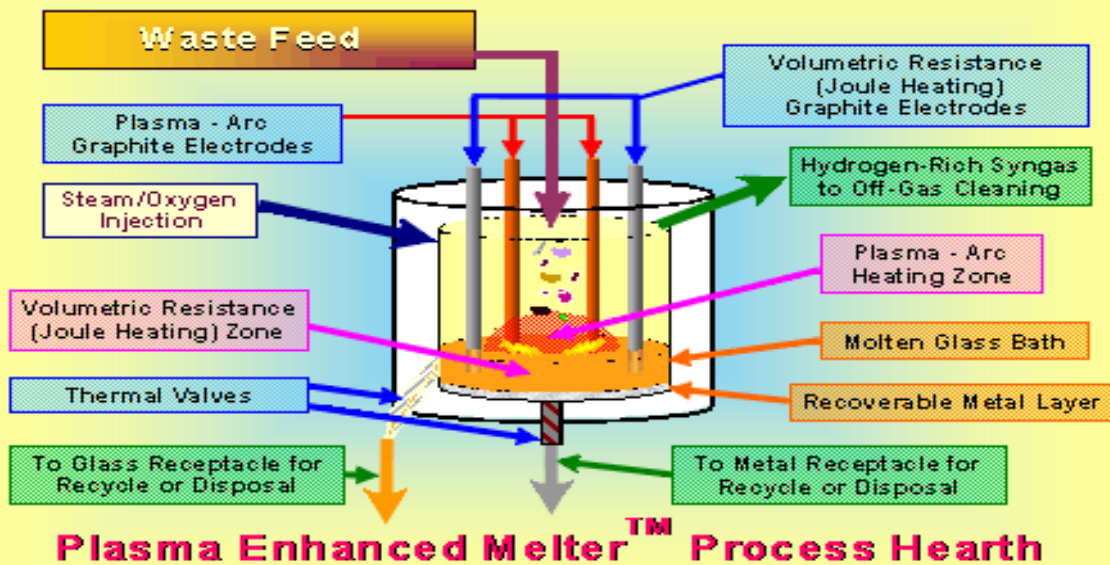
## Technology

### The IMG-Technology

### What for is the IMG-Technology?



# Plasma Enhanced Melter—Dow Corning 20t/d



# PEAT-Plasma Energy Applied Technology

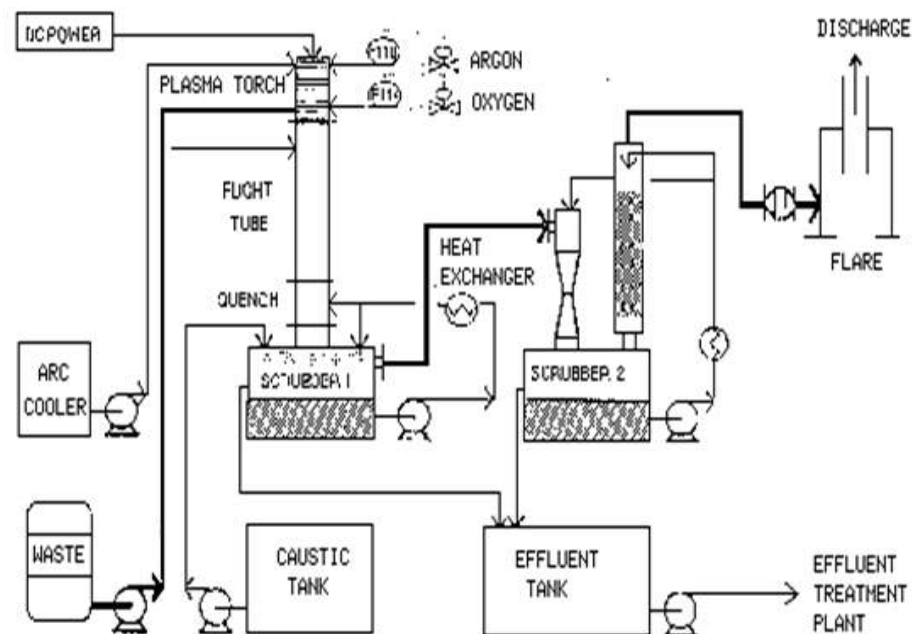
## ❖ PTDR-100 – Sacramento, CA





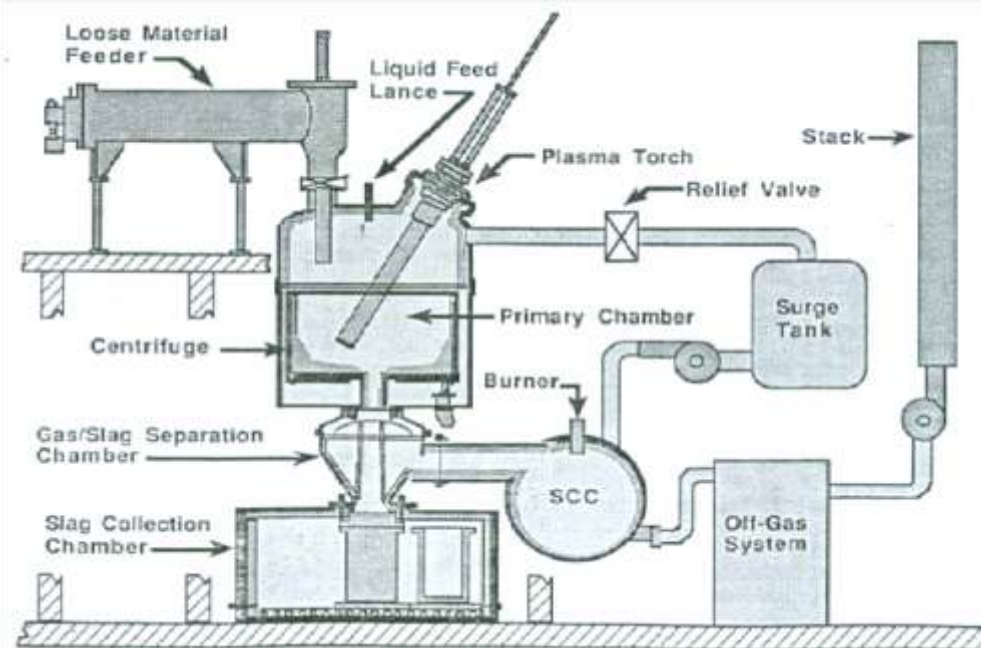
# PLASCON™—for gas and liquid POPs

- ❖ In-Flight Plasma Arc System
- ❖ Australian CSIRO and SRL Plasma



# PACT™

- ❖ PACT—Plasma Arc Centrifugal Treatment
- ❖ Retech Systems LLC



# Plasma Convert System

- STARTECH
- Air torch
- Chemical Weapon
- 200-2000 kW
- Power generation
- Not commercialized
- 2000 in China





# Many companies in the world

- ❖ US Solana
- ❖ French Aerospatial Espace & Defence
- ❖ Israel EER-Plasma Gasification Melting
- ❖ US Scientific Utilization, Inc. – Russian
- ❖ Munster II – CW PLASMOX<sup>®</sup> RIF-2, PLASMARC<sup>®</sup>
  
- ❖ French EUROPLASMA
- ❖ US Phoenix
- ❖ Swedish ScanArc –EER + KTH

# Development of Plasma Arc Technology in Waste treatment Group, CAS- IMECH

AC plasma arc metallurgy technology from later 1980s to 1995, it is used to treat hazardous wastes after 1995.



# DM Destruction-2002

- DM (Adams)  $C_{12}H_9NClAs$  + Additives
- 2002-3-30 As: 3-5% in Bottom Ash
  - As; 35% in Ash, 65% in Off-gas (Soot)
- 2002-9-27, 20-30kg/h, Glass well

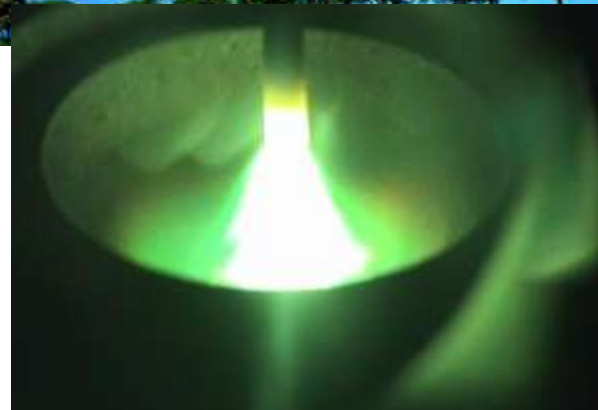


30kW DC plasma arc reactor was set up in 2006



It is used to study the formation mechanism of the vitrified slag, the transfer mechanism of hazardous elements and the formation mechanism of gaseous Pollutants. Various hazardous wastes have been destroyed and vitrified with this reactor.

# 30 kW DC Plasma Arc Reactor





# Plasma System-3t/d in Lab, 2007

Feeding  
Hydrogen gas supply  
Reactor  
Residue Discharging  
Off gas Cleaning  
Special Transformer  
Plasma Generator  
Control and Metering





## Vitrified Slag

- ❖ The solid residues of toxicant and additives forms vitrified slag if the cooling speed is high enough
- ❖ ste.

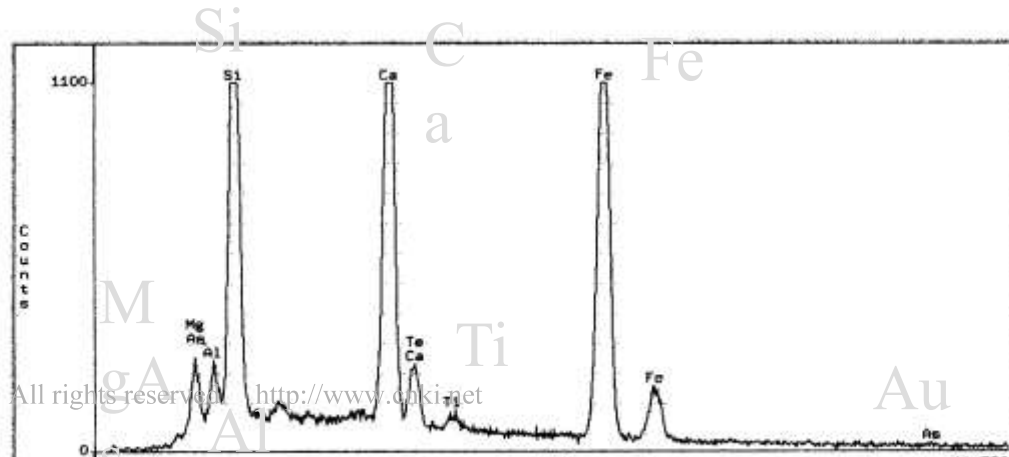
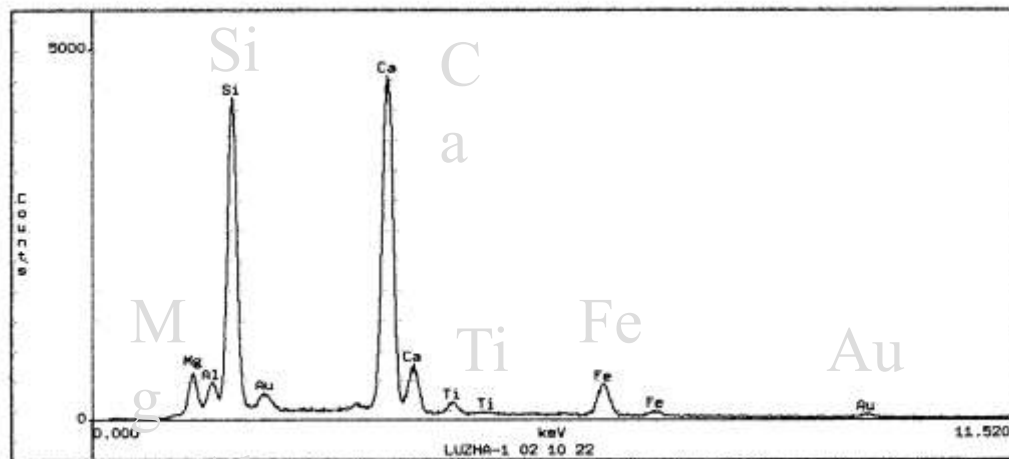


## Not Vitrified Slag

- ❖ The slag from CW-2 is incompact and mat, quenching rate – key factor
- ❖ Compositions of Additives – Important
- ❖ Energy Consumption: 1.0 to 1.2 kW-hr/kg
- ❖ Reductive environment, off-gas: 20% of conventional incineration



# Glass Content by VANTAG Energy Spectrometer



# I.Mech.CAS – ChenGuang-3t/d

The First Industry-scale Plasma Chemical Waste Treatment System in China



- Disposal of hazardous wastes such as chemical wastes, solid POPs, etc.;
- Provided with integrated feed-in sub-system and PC control system;
- The DC power supply of plasma generator is 150 kW;
- Argon is employed as the reaction gas;

- HCl recovered.

# ChenGuang-2006





## 5-10t/d Demo in Shaanxi – 2008/9

- ✓ Plasma Arc Reactor — 400 kW AC/DC, Graphite
- ✓ Afterburner — soot, HCl
  - ✓ High T >1400°C, corrosion, refractory?
- ✓ Heat exchanger — gas cooling
  - ✓ Corrosion: HCl > 320°C, < 160°C
- ✓ Quencher — 600°C —> 160°C, Dioxin reduction
- ✓ Wet scrubber — corrosion, waste water
- ✓ Baghouse: soot and fly ash
- ✓ Carbon bed: PCDD/Fs

# Pre-Treatment





# Off-Gas Treatment



二燃室、换热器、冷却  
塔、除尘器、活性炭、  
脱酸塔、碳床、引风机



# Tem. in off-gas/reactor-outwall



# Emmision Tested-2010.7/2011.4

No.	污染物 Pollutents	单位Unit	GB18484-2001(按kg/h处理能力)			Tested
			≤300	300~2500	≥2500	
1	烟气黑度	林格曼	1级			1级
2	烟尘(dust)	mg/m <sup>3</sup>	100	80	65	12.1
3	一氧化碳 (CO)	mg/m <sup>3</sup>	100	80	80	22.5
4	二氧化硫 (SO <sub>2</sub> )	mg/m <sup>3</sup>	400	300	200	ND
5	氟化氢 (HF)	mg/m <sup>3</sup>	9.0	7.0	5.0	待测
6	氯化氢 (HCl)	mg/m <sup>3</sup>	100	70	60	13.64
7	氮氧化物 (NOx)	mg/m <sup>3</sup>	500			636
8	汞Hg	mg/m <sup>3</sup>	0.1			ND
9	镉Cd	mg/m <sup>3</sup>	0.1			ND
10	砷 As、镍Ni	mg/m <sup>3</sup>	1.0			0.056
11	铅 Pb	mg/m <sup>3</sup>	1.0			0.029
12	Cr、Sb、	mg/m <sup>3</sup>	4.0			待测
13	PCDD/Fs	ng/m <sup>3</sup>	0.5 (TEQ)			0.39

# Residues - 2010-7-15

序号	危害成分	浸出液中危害成分浓度限值 (mg/L)	测定值
无机元素及其化合物			
1	铜 (Cu)	100	0.04
2	镍 (Ni)	100	待测
3	镉 (Cd)	1	0.005
4	铅 (Pb)	5	0.1
5	总铬(Cr)	15	0.018
6	铬 (Cr6+)	5	0.004
7	烷基汞(Alkane Hg)	不得检出	未检出
8	汞 (Hg)	0.1	待测
9	铍 (Be)	0.02	待测
10	钡 (Ba)	100	待测
11	钴 (Ni)	5	0.04
12	总银(Ag)	5	0.01
13	砷 (Ar)	5	3.6
14	硒 (Se)	1	待测
15	无机氟化物 (F-)	100	2.87
16	氰化物 (CN-)	5	0.003



## Applications, Chinese Technologies.

- ❖ Solid Wastes: FlyAsh, MW, ChemicalWaste, CW
- ❖ HW: CAS-IMECH—Chenguang, Liquan 10t/d
- ❖ MSW: Huanwei Group
- ❖ Waste Water
  - Sichuan Normal Univ. Waste Water in Pulp Mill
  - Zhejiang Univ. Slide Arc Plasma for Organic Waste Water
  - South-West Institute for Nuclear Physics
- ❖ Waste Gas – many
- ❖ Igniting Boilers Without Oil—Longyuan Group
  - Save oil fuel

# Non Plasma Technology

## —Electric Heating with Gas Engines

- ❖ From Plasma Tech, Heat transfer difficult
- ❖ **1100'C, 10s, no ActiveCarbon**
  - SynGas 14.1MJ/m<sup>3</sup>, 3370 kcal/m<sup>3</sup>
  - PCDD/Fs **0.007ng/m<sup>3</sup>(TEQ)**
- ❖ 1200kW-h/t(treated waste)



# Conclusions

- ❖ Plasma gasification is the state-of-the art technology for waste treatment, and with excellent environmental impact, Ultra Low PCDD/Fs can be obtained for every sorts of wastes
- ❖ T is the most important factor, syngas can be **heated up to 1100'C using less energy**
- ❖ Syngas residence time can be more than 5s
- ❖ Water quenching cannot be used, since reductive condition is reducing PCDD/Fs regeneration
- ❖ Electric Heating (Non Plasma) is also for Ultra Low PCDD/Fs, as well as Plasma Technologies
- ❖ BiJie, Guizhou Project has started in April 2014

# Thank You !

$O/Si$  in the range of 2~3

is appropriate to form the vitrified slag