Fly Ash Catalyzed Mercury Oxidation Chlorination Reactions

Sukh Sidhu

Graduate Student: Patanjali Varanasi

Environmental Engineering
University of Dayton, 300 College Park
Dayton, OH 45469-0132

Sidhu@udri.udayton.edu

2007 UCR HBCU/OMI Contractors Review Conference
June 6, 2007

Introduction

- Strict EPA regulations for mercury control.
- Mercury control depends on the speciation of mercury.
- Gas phase reactions don't influence the effluent mercury speciation.
- Surface reactions in the post combustion zone control mercury speciation in stack gases.
- Surface composition plays an important role in mercury transformation.
- Study of mercury transformation in the post combustion zone is important to determine the speciation of mercury.

Possible Mercury Transformation Reactions in Combustor Cool Zone

- Oxidation
  - Activated Carbon
  - Fly Ash
  - Surface Oxygen Complexes
- Chlorination
  - HCl (poor chlorinating agent)
  - Conversion of HCl to Cl_2 (Deacon Reaction)
  - Role of Metals

Role of Surfaces

- Adsorption

- Dependence on carbon/calcium content

- Catalysis

- Dependence on metal content

Surfaces play an important role in mercury transformation reactions

Objectives

- Understand how fly ash surface and composition of flue gas affect mercury speciation, partitioning, and reactions under post-combustion zone conditions.

- Use this knowledge to develop a predictive tool that could estimate mercury speciation based on fly ash characteristics and composition of flue gas.

Experimental Approach

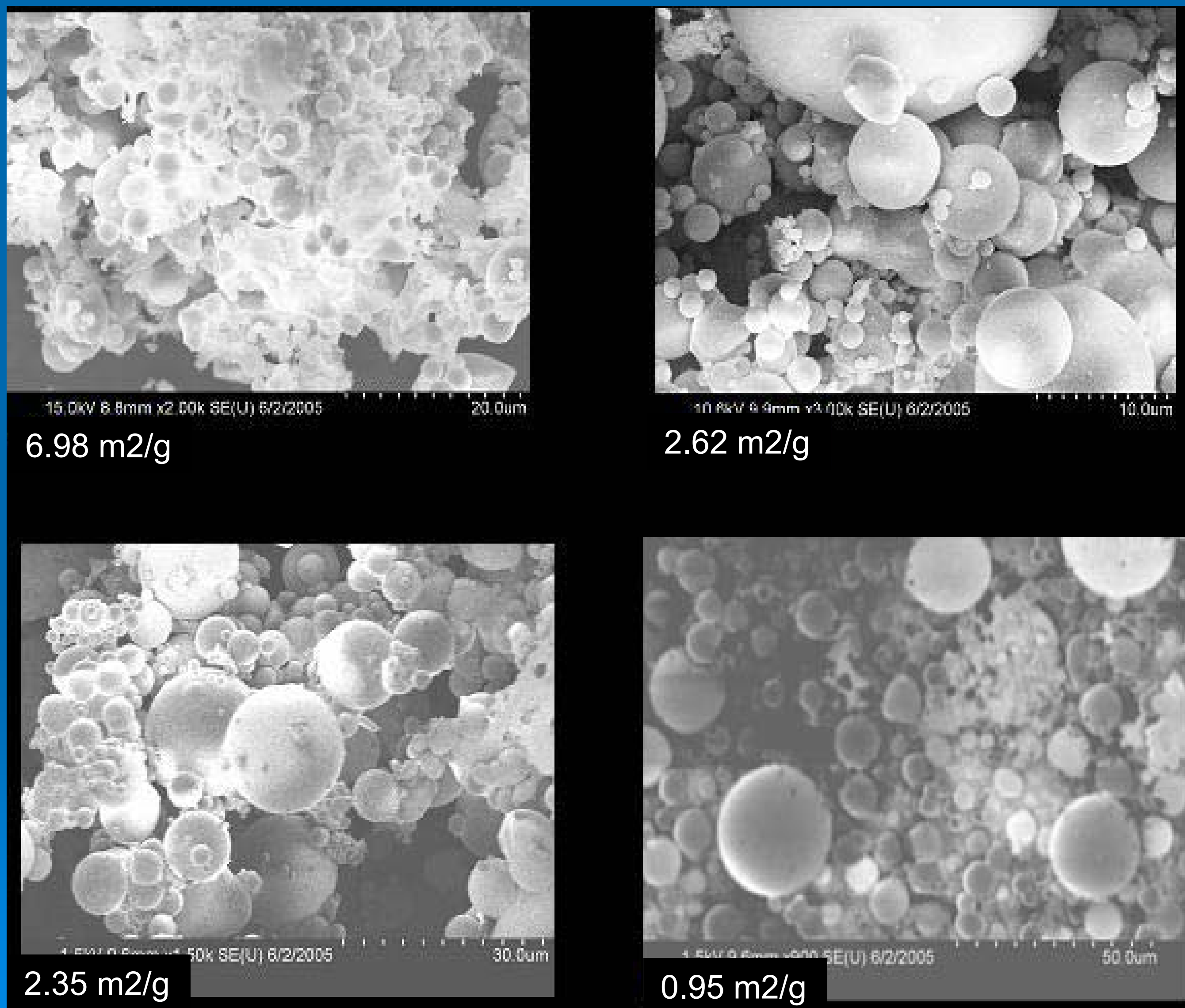
Our Experimental approach is based on previous surface catalyzed cool zone pollutant formation studies.

- Fly ash is a very complex surface – do extensive characterization.
- Obtain preliminary data on mercury transformation reactions using coal fly ashes. Use these results to determine the range of catalytic activity of coal fly ashes in mercury transformation reactions.
- Correlate fly ash composition and flue gas composition with observed catalytic activity.
- Divide overall mercury transformation process into several manageable reaction systems. Use model fly ashes to validate observed correlations.

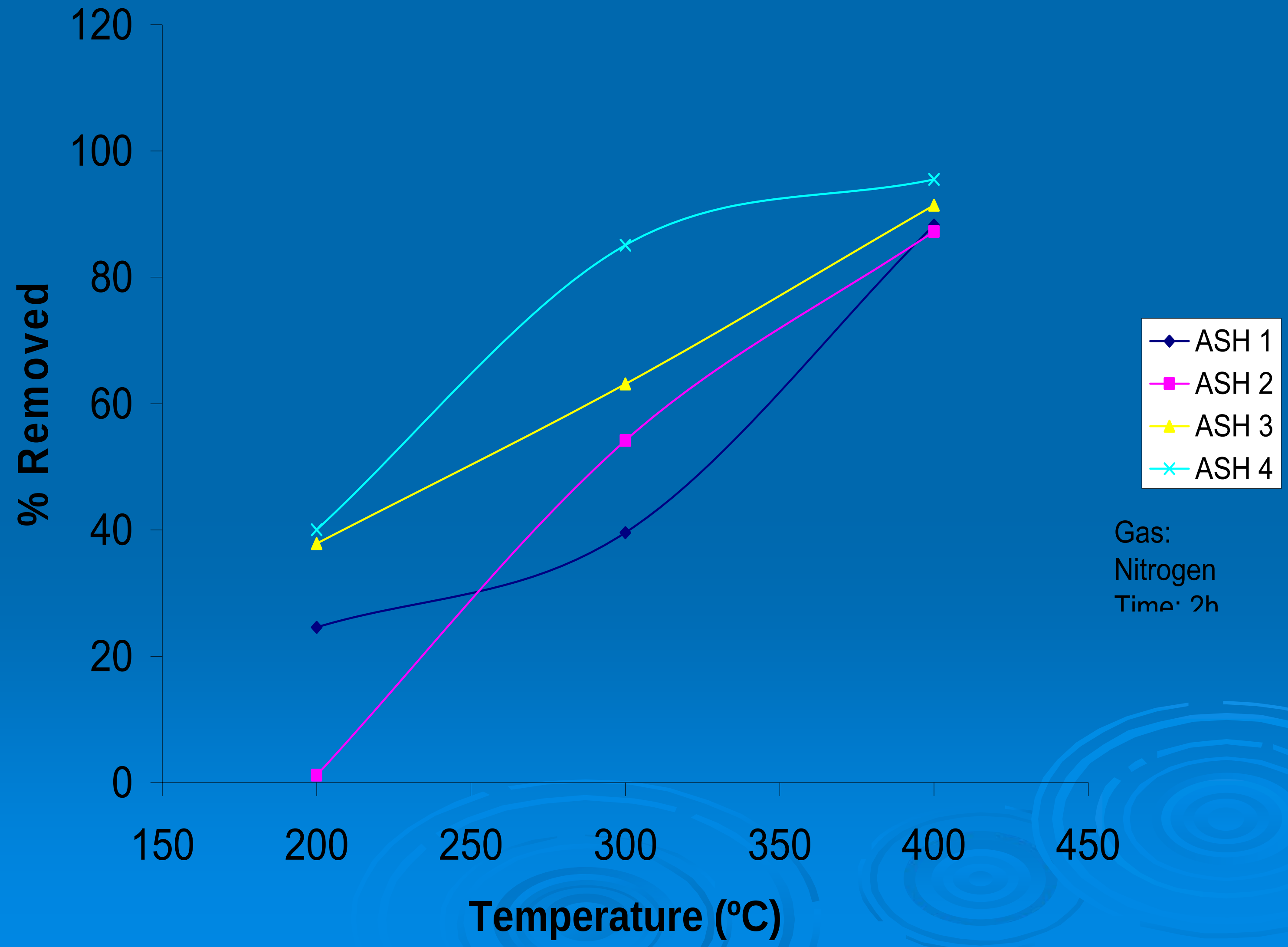
Elemental Analysis of Fly Ashes (EDS)

Ash	Mg	Al	Si	K	Ca	Ti	Fe	O	S	Na	P	SA (m2/gm)
1	0.59	14.8	26.64	2.69	0.75	1.38	4.84	47.72	0.35	0.19	0.06	6.98
2	0.5	15.4	26.72	2.96	1.18	1.07	3.81	47.84	0.22	0.32	0.05	2.62
3	0.92	14.27	26.29	2.86	2.32	0.92	4.17	47.32	0.28	0.56	0.11	2.35
4	2.53	10.11	19.72	0.86	14.94	1.08	4.08	43.83	0.86	1.26	0.73	0.95
5	0.42	12.67	21.79	1.95	2.59	0.63	14.43	43.97	0.72	0.57	0.26	0.7
6	0.64	11.4	21.59	1.56	2.7	0.94	13.69	44.04	1.44	1.92	0.08	0.82
7	0.44	11.91	19.57	1.69	2.64	1.11	14.05	43.85	2.22	2.2	0.33	0.78
8	0.46	12.09	22.17	1.98	2.2	0.71	14.53	43.87	0.77	1.16	0.08	0.55
9	0.41	10.86	21.01	1.57	2.36	0.9	14.09	44.1	2.22	2.34	0.14	0.86
10	0.44	11.48	21.24	1.85	2.45	0.73	16.15	43.21	0.86	1.38	0.21	0.54

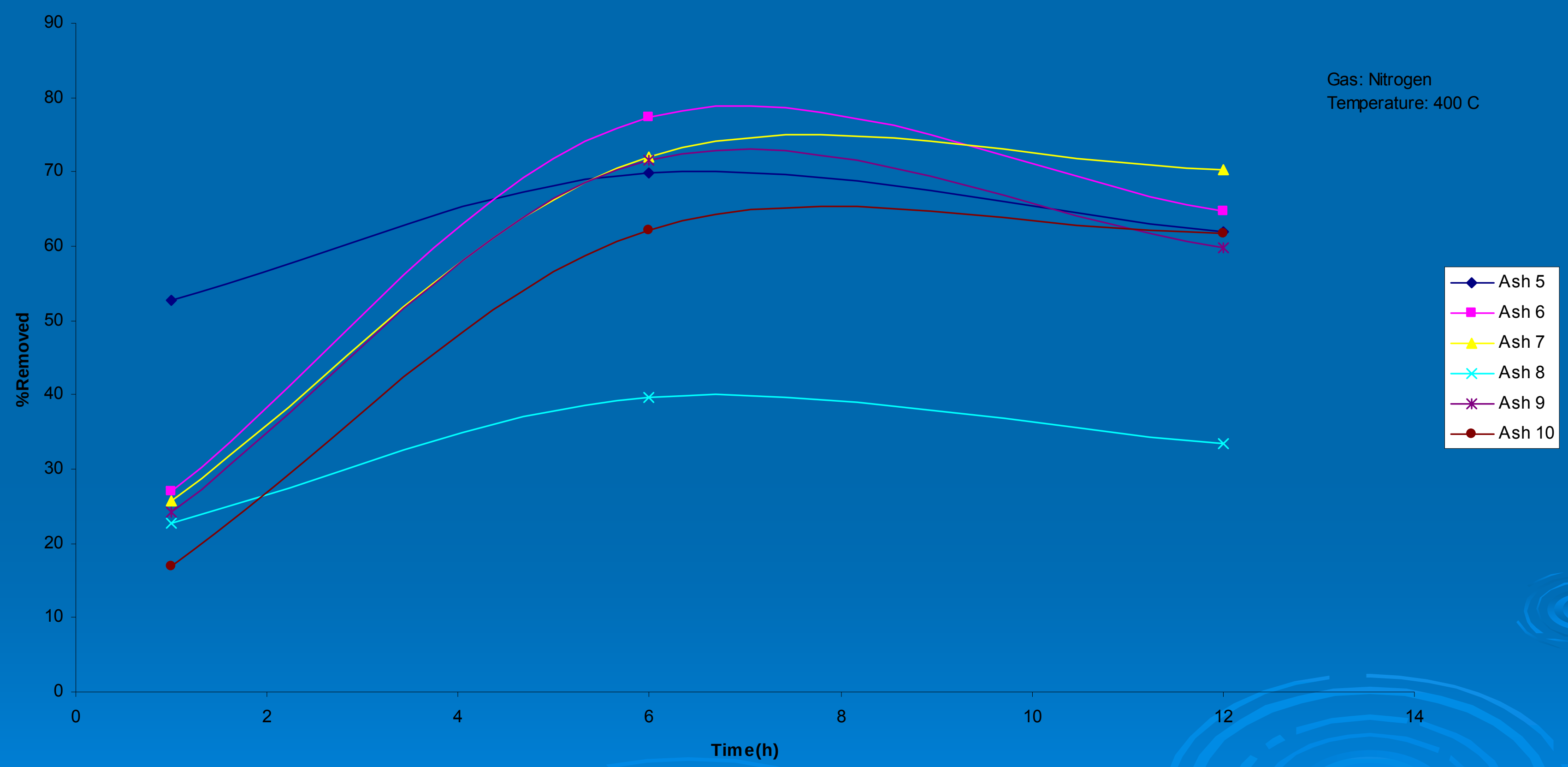
High Resolution SEM of Ash Samples



Mercury Desorption

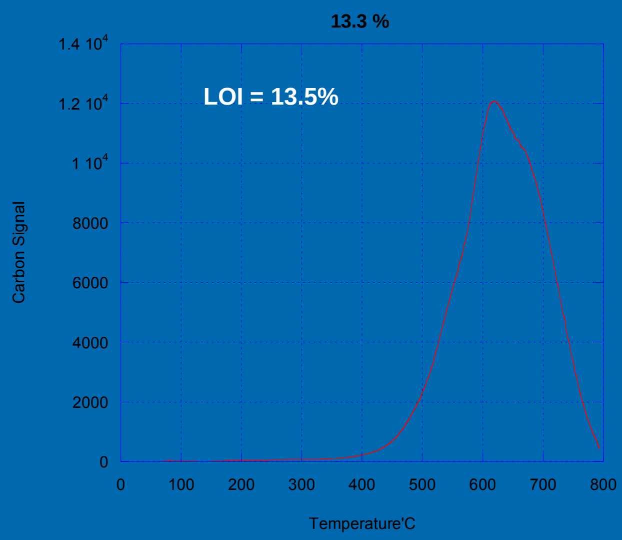


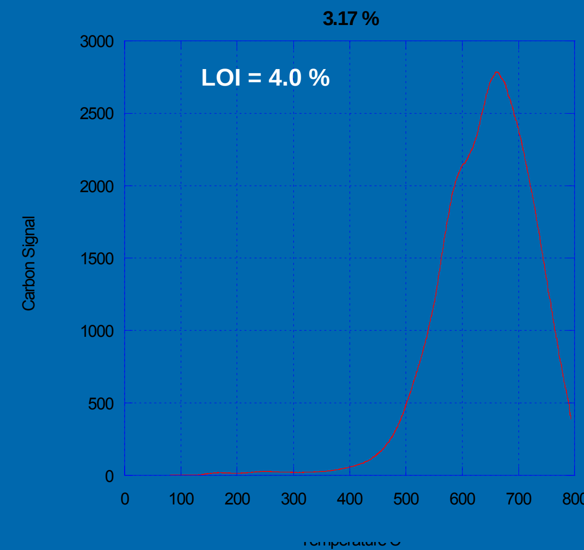
Mercury Desorption at 400ºC

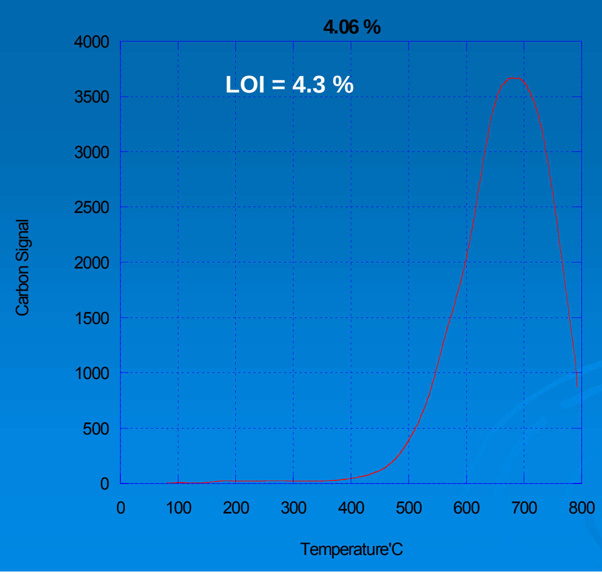


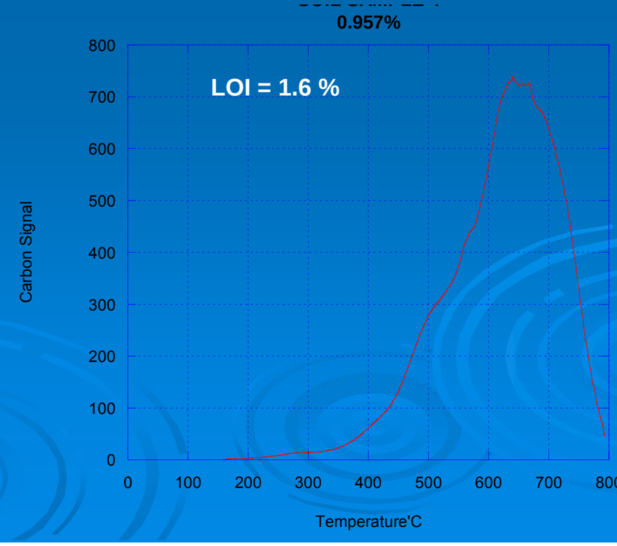
Carbon Analysis

Fly Ash Sample	1	2	3	4	5	6	7	8	9	10
Carbon Content (%)	13.5	4.0	4.3	1.6	1.5	1.4	1.2	1.4	1.3	1.3





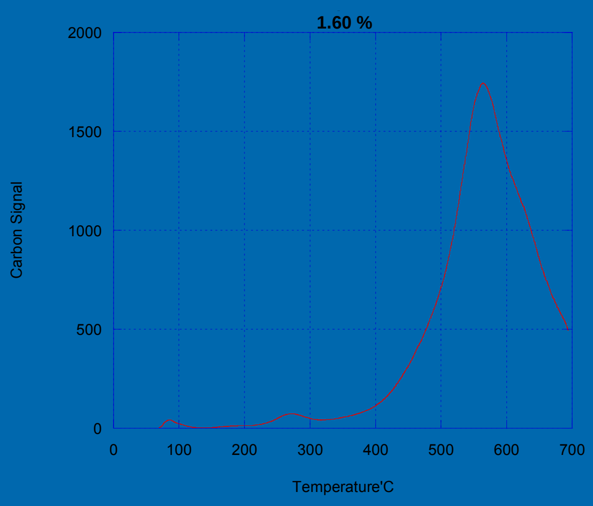


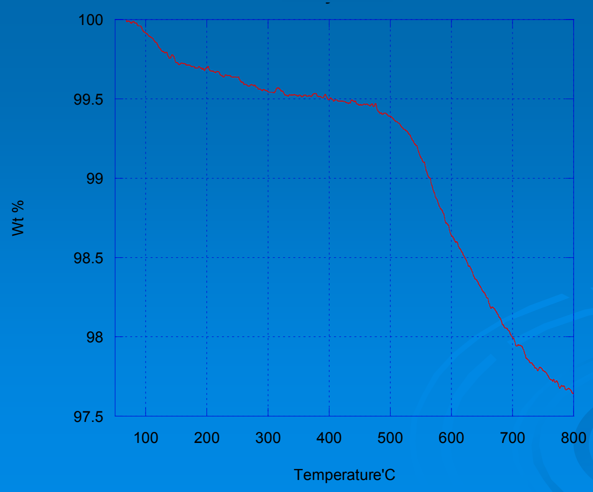


Thermo Gravimetric and LECO Analysis of Original and Desorbed Fly Ash

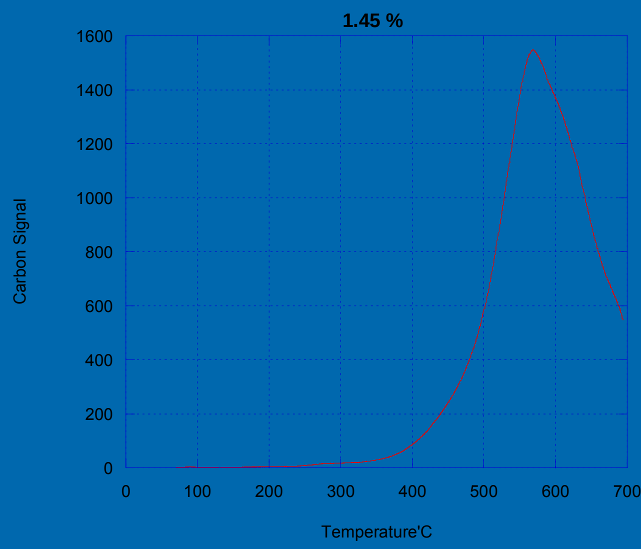
LOI = 1- 1.5%

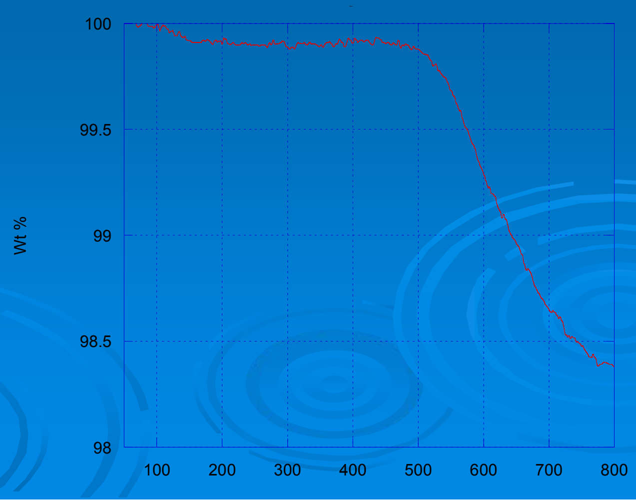
Ash 7 Original



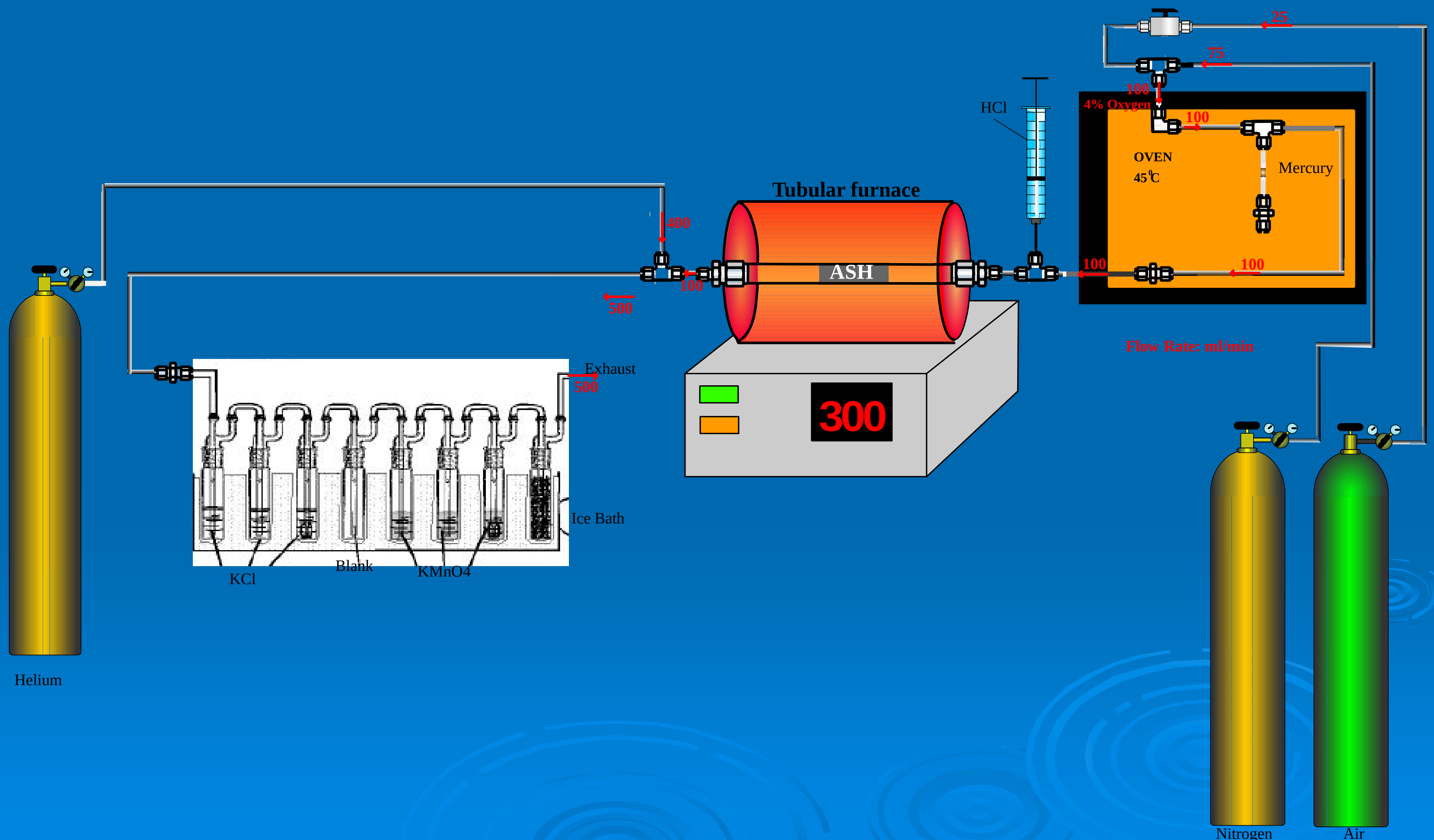


Ash 7 Desorbed

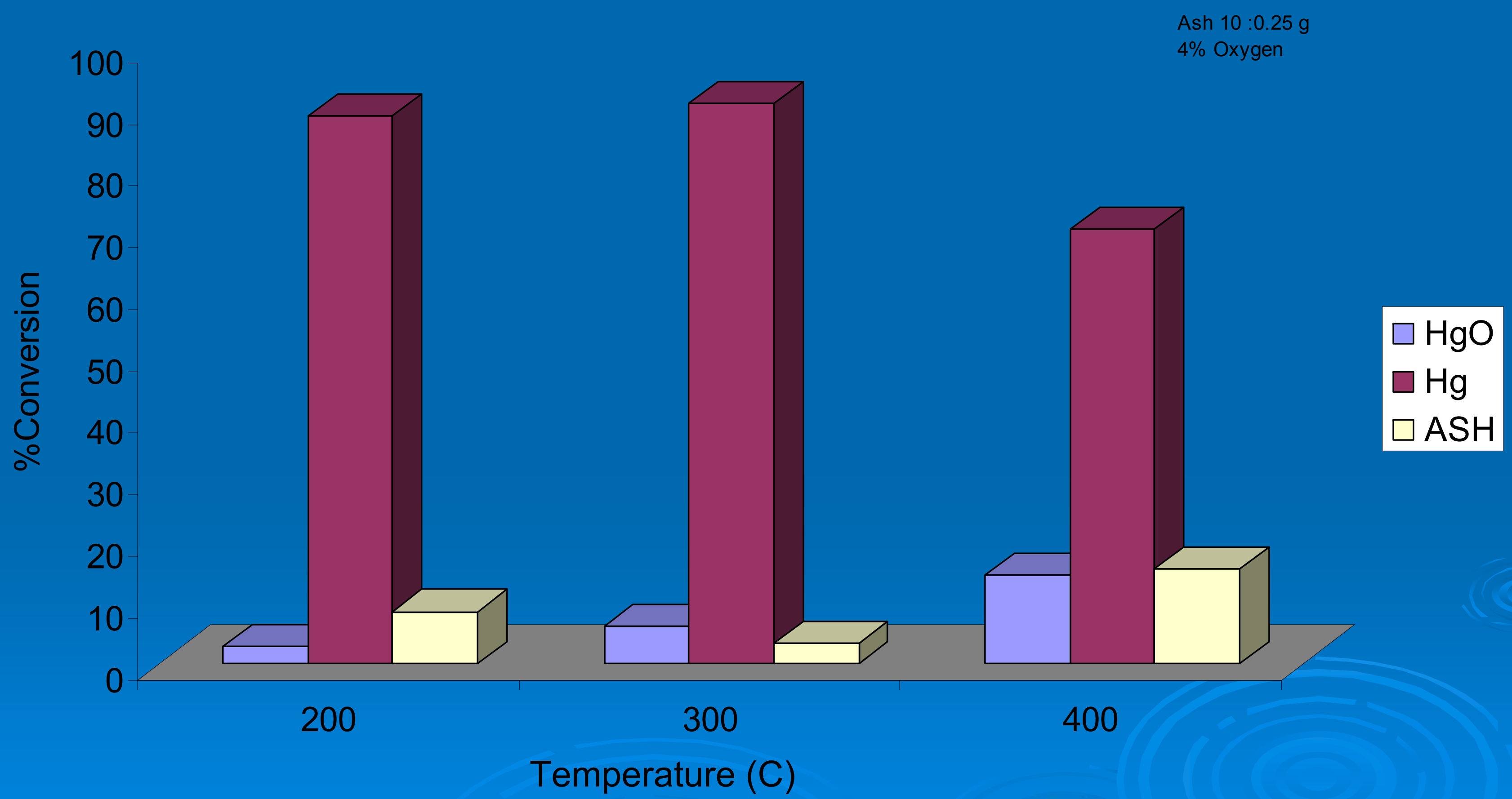




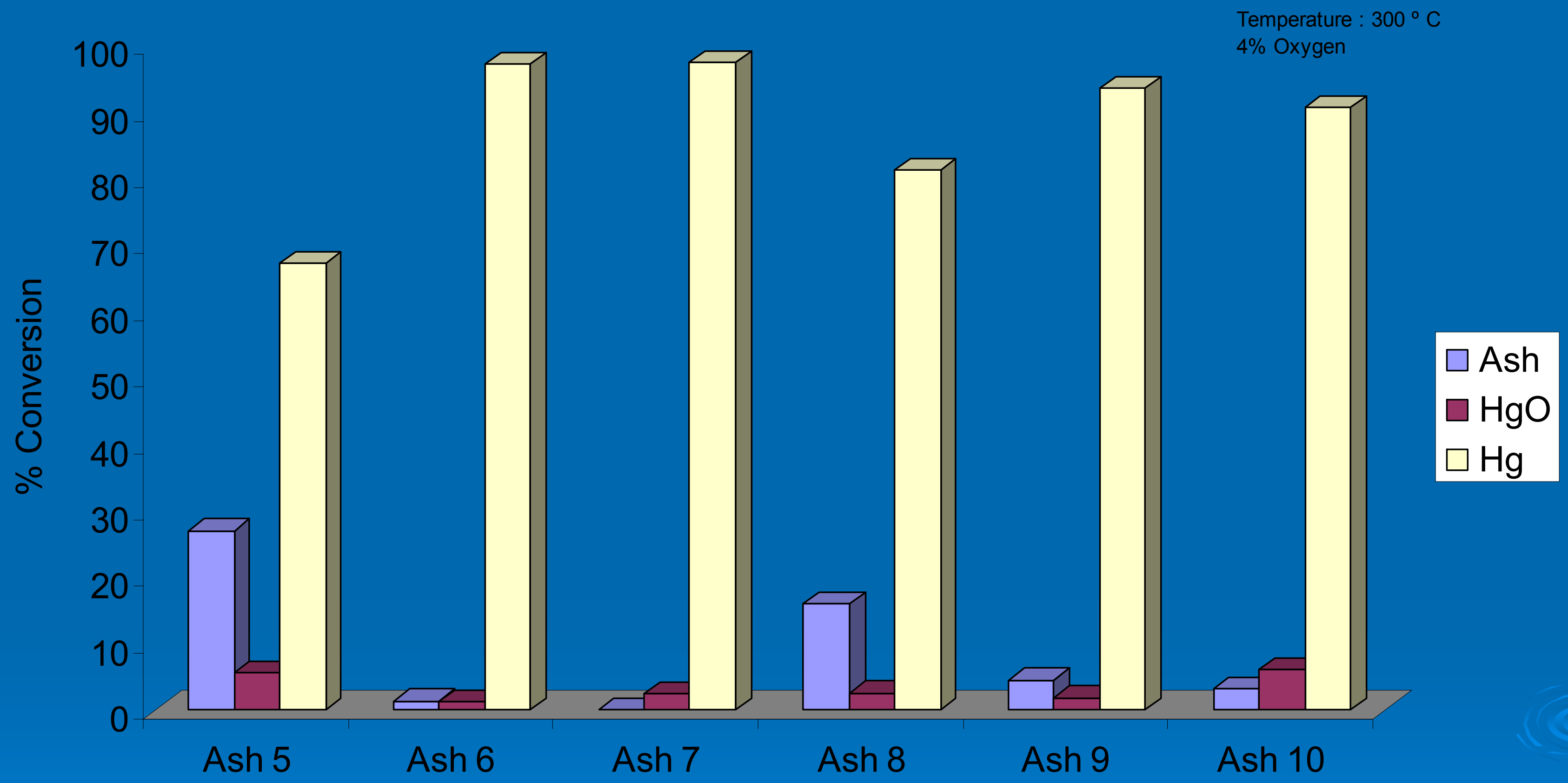
Experimental System



Conversion of Mercury at Different Temperatures

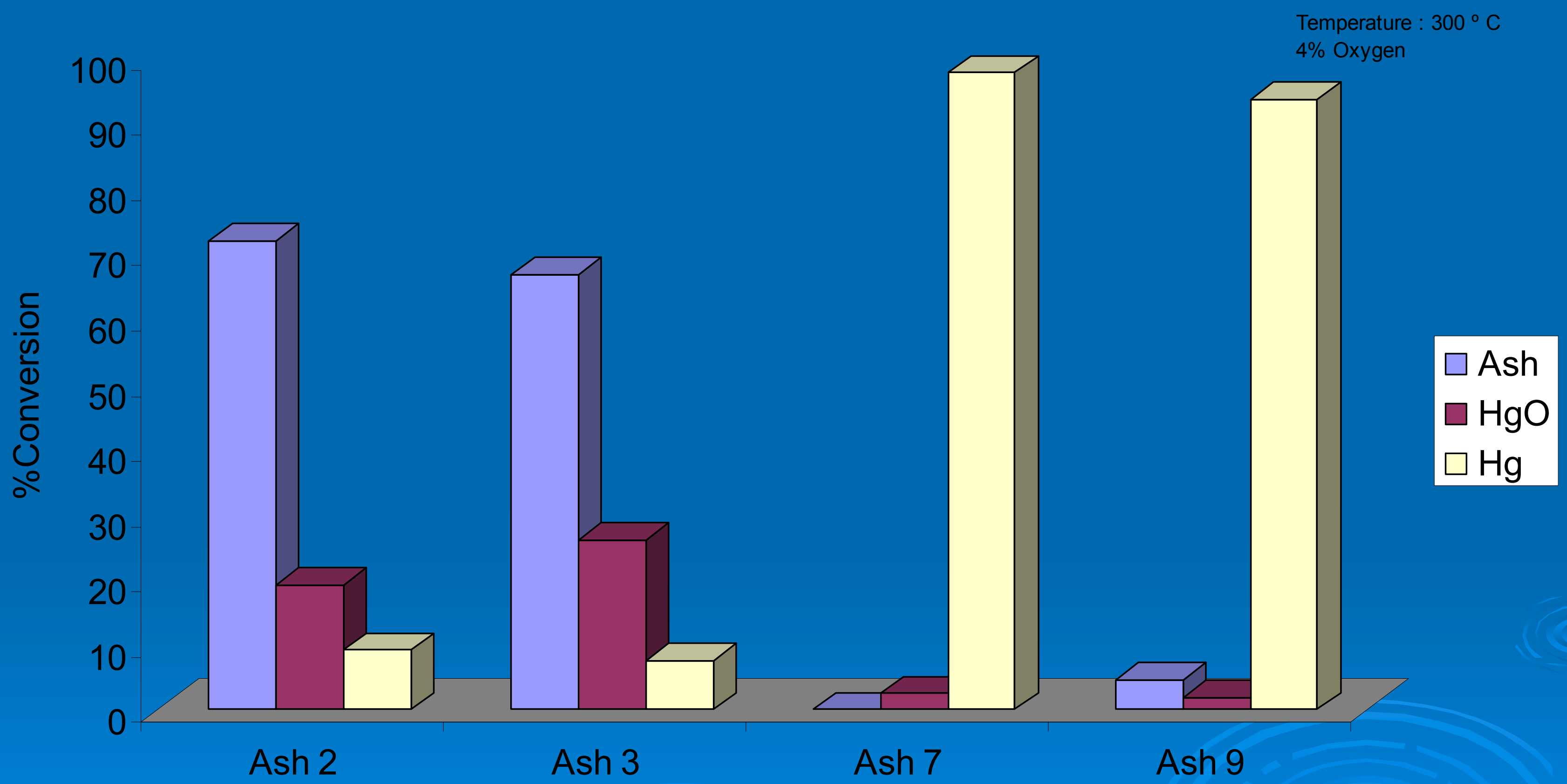


Mercury Oxidation (same plant)

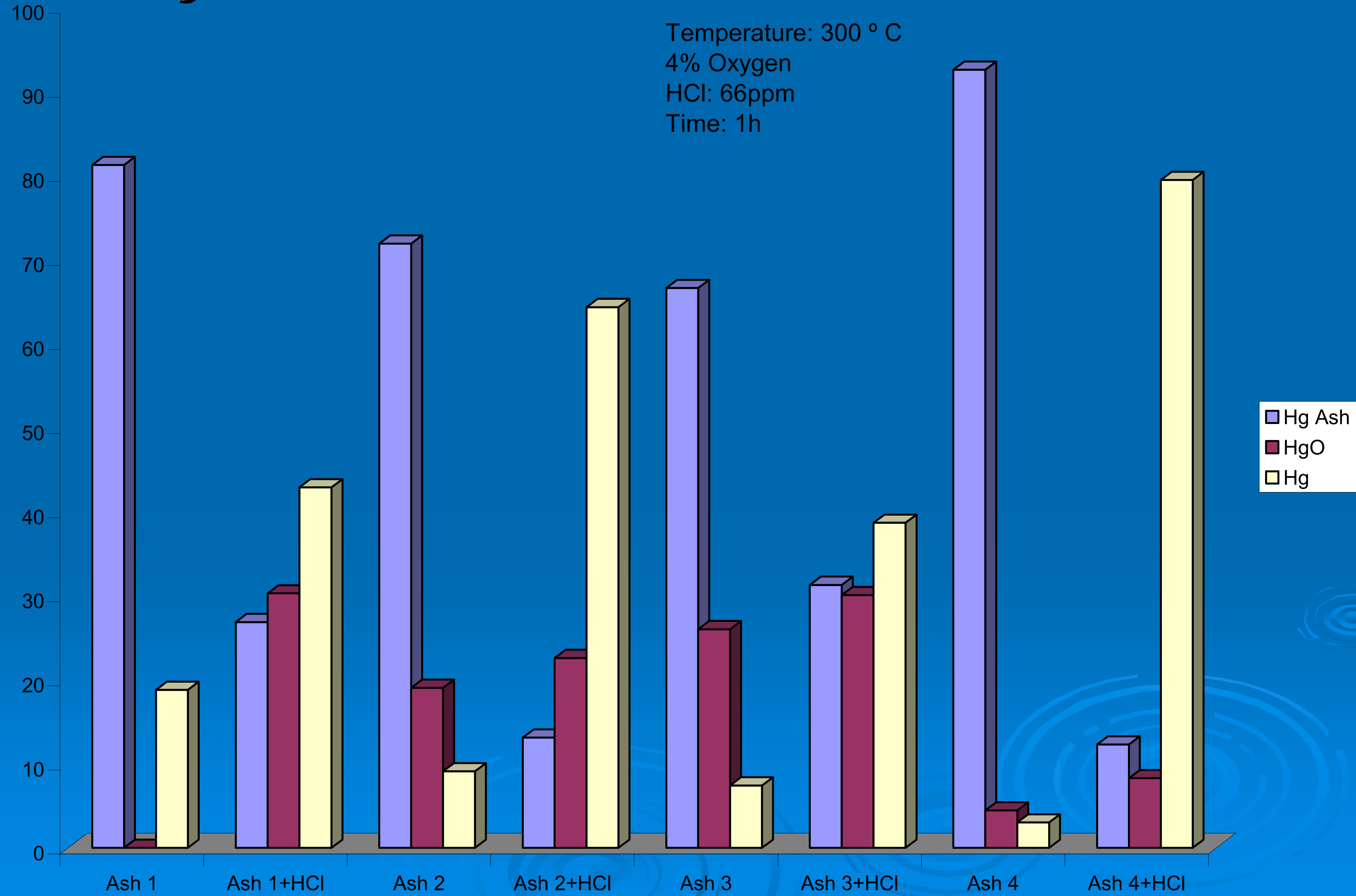


	Ash 5	Ash 6	Ash 7	Ash 8	Ash 9	Ash 10
Unit	2	2	2	2	2	2
Date	3/14/2006	3/15/2006	3/15/2006	3/16/2006	3/16/2006	3/17/2006
Time	13:00	8:55	13:00	8:00	13:00	8:00

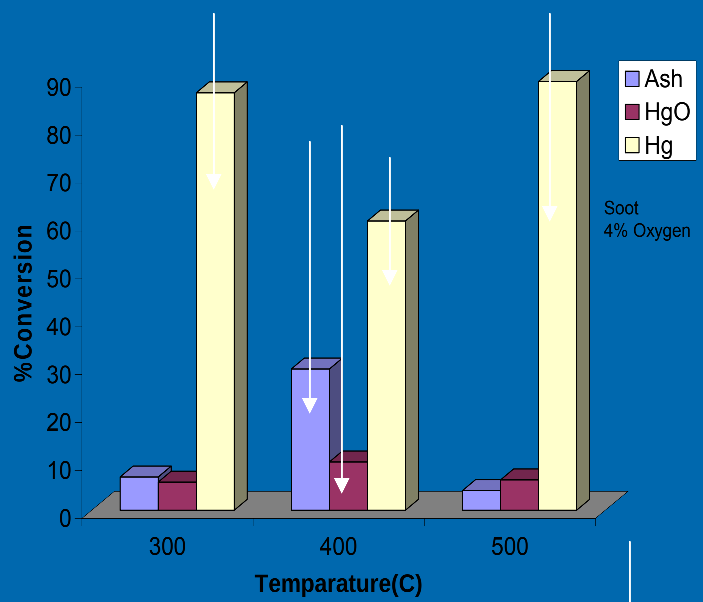
Mercury Oxidation (Different Plants)

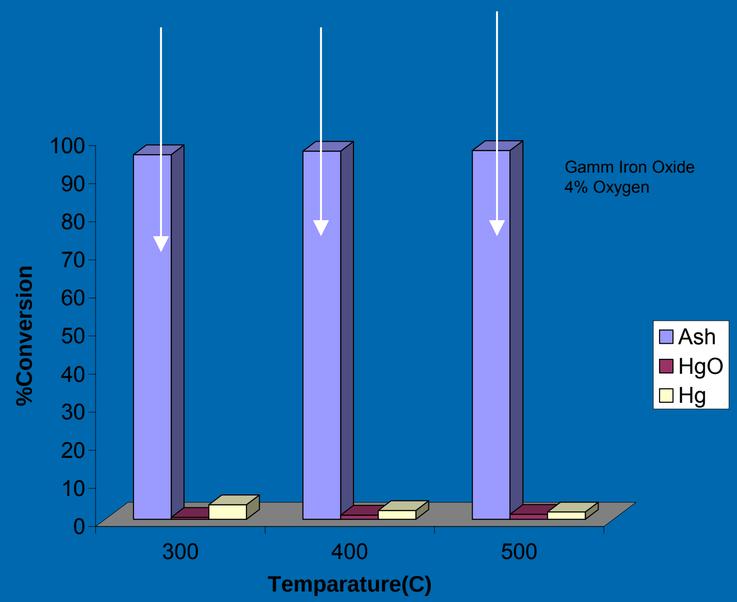


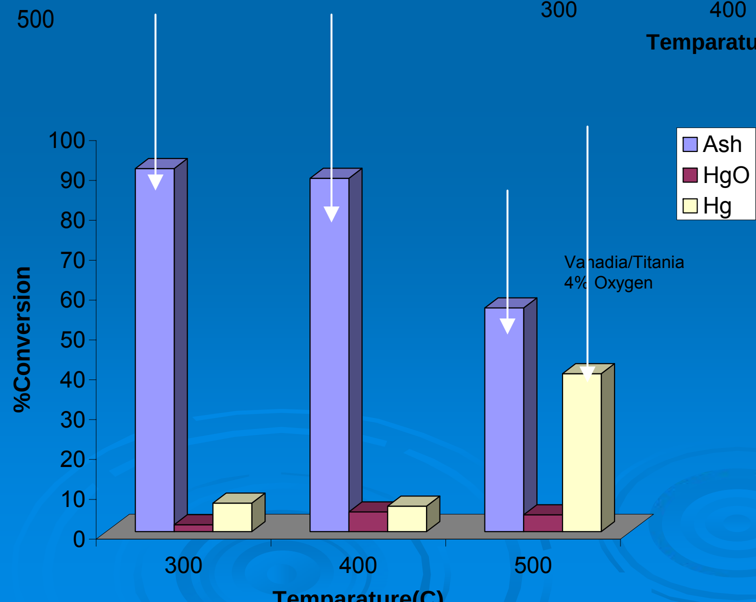
Impact of HCl
Fly Ashes from Different Plants



Surface Catalyzed Transformation at Different Temperatures







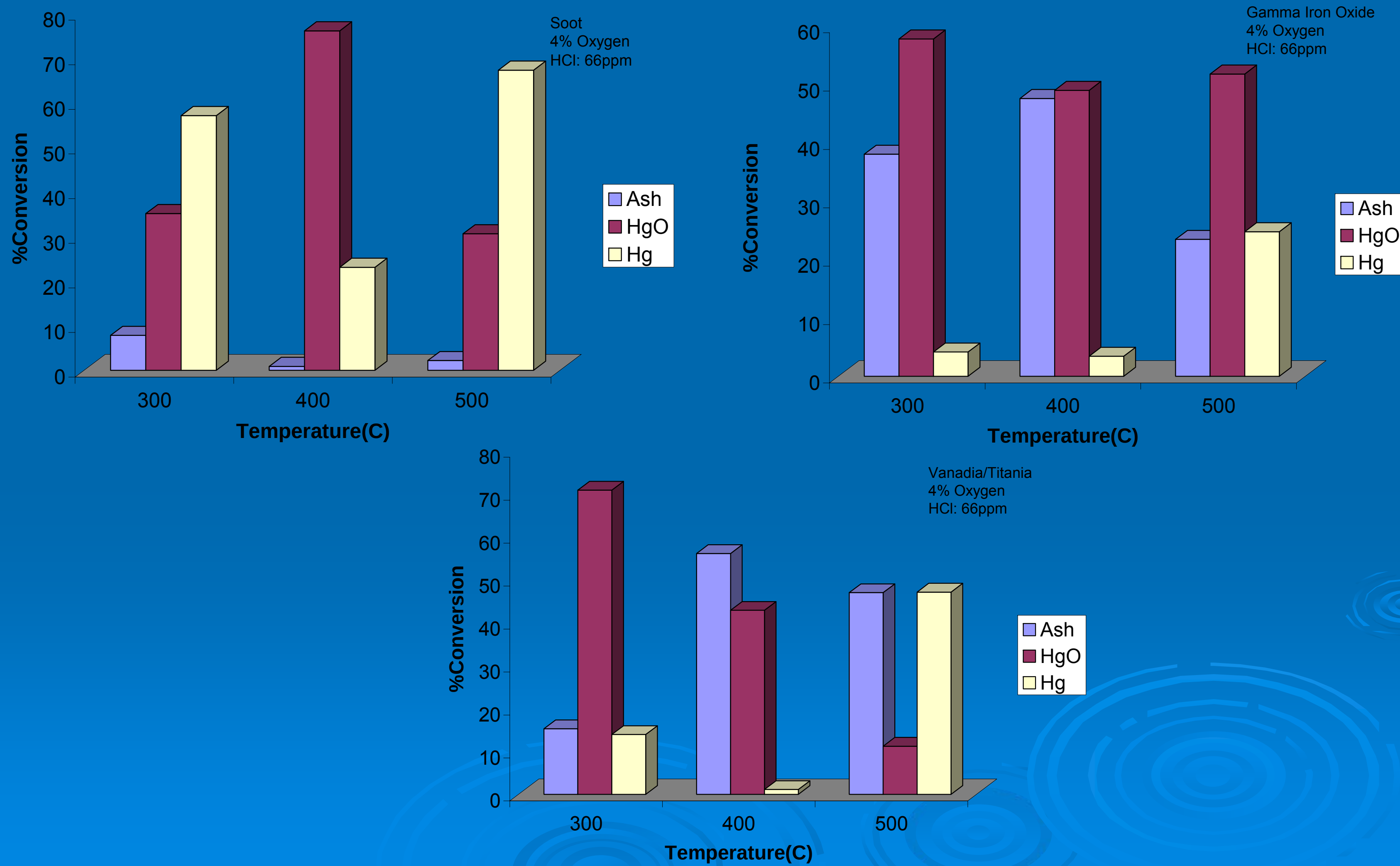
Surface Catalyzed Transformations : Presence of HCl

- HCl not a good oxidizing agent
- But in the presence of surface it is converted to chlorine: Deacon Reaction

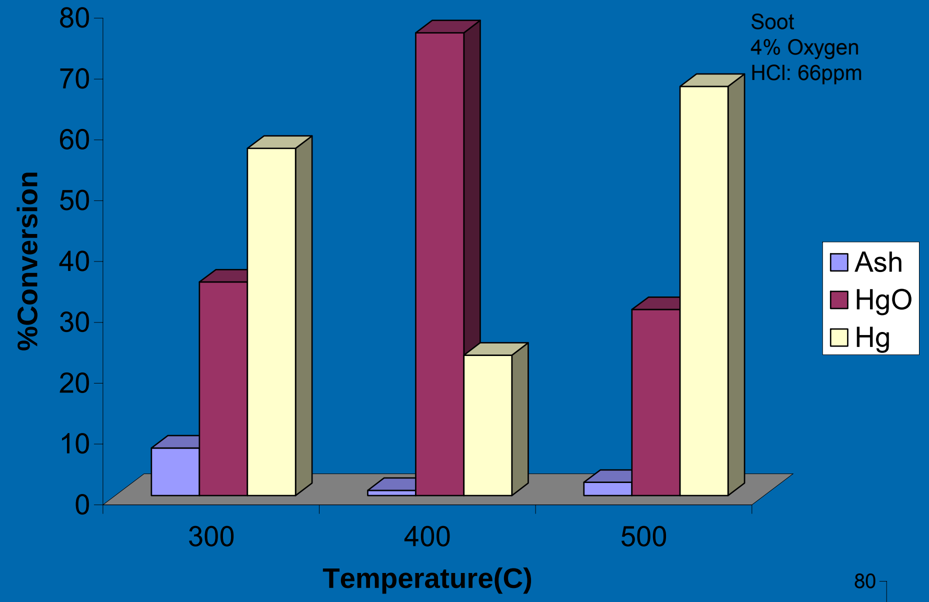
$$2HCl + 2O_2 \longrightarrow H_2O + Cl_2$$

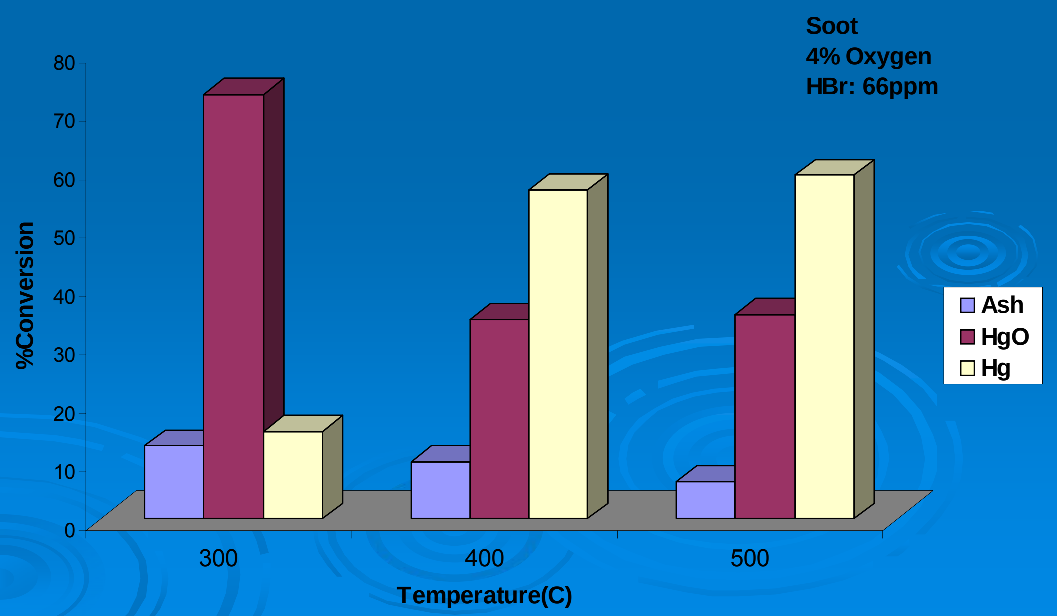
- Chlorine better oxidizing agent.

Surface Catalyzed Transformations : Presence of HCl

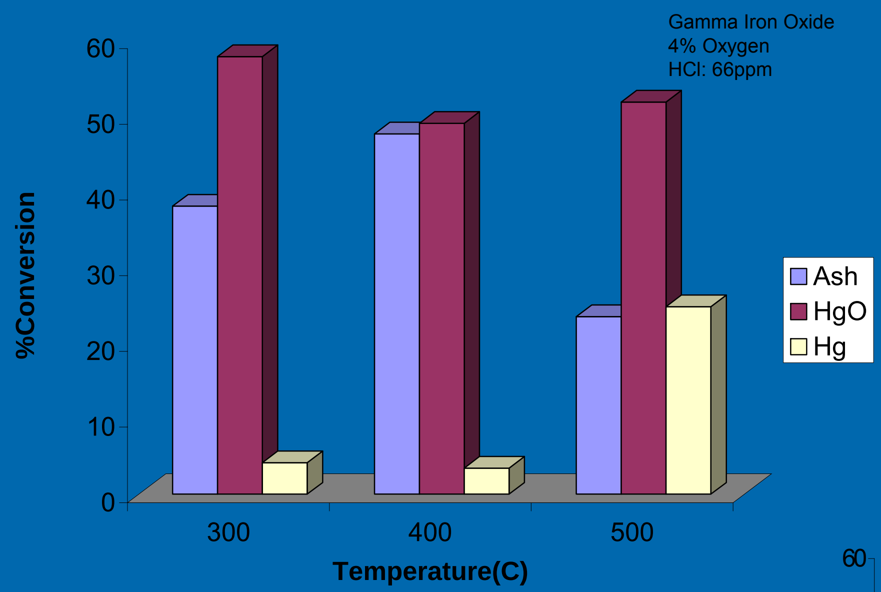


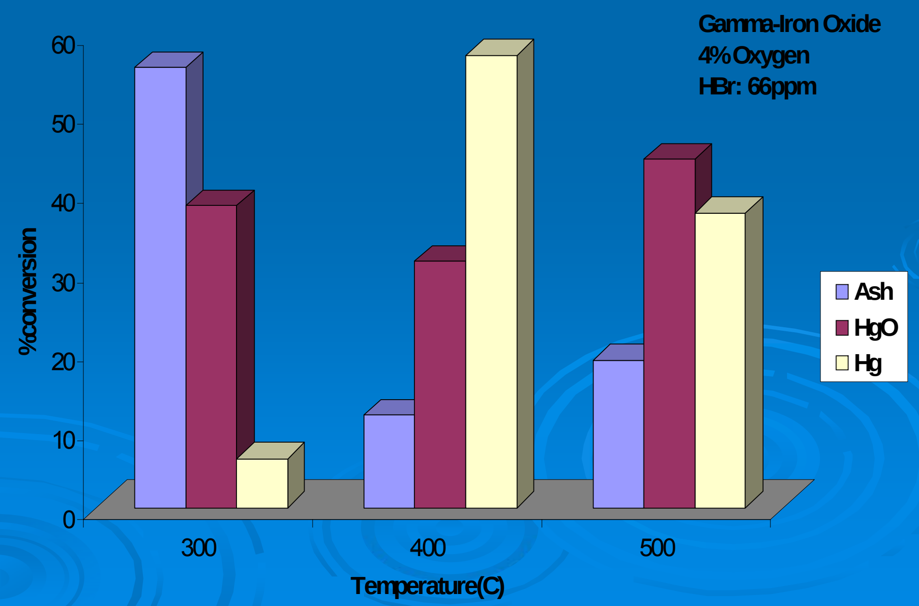
Surface Catalyzed Transformations : HCl vs HBr



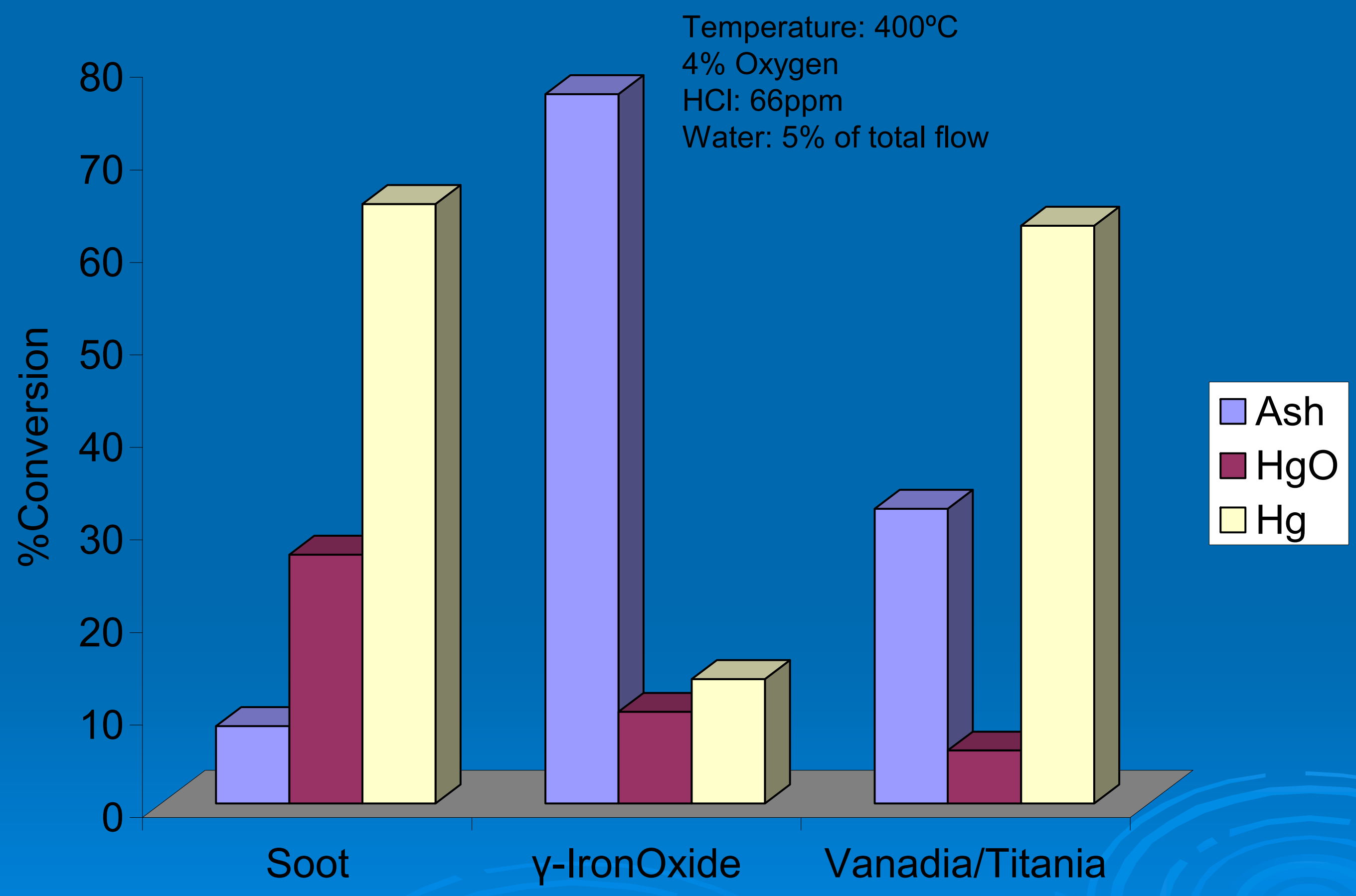


Surface Catalyzed Transformations : HCl vs HBr

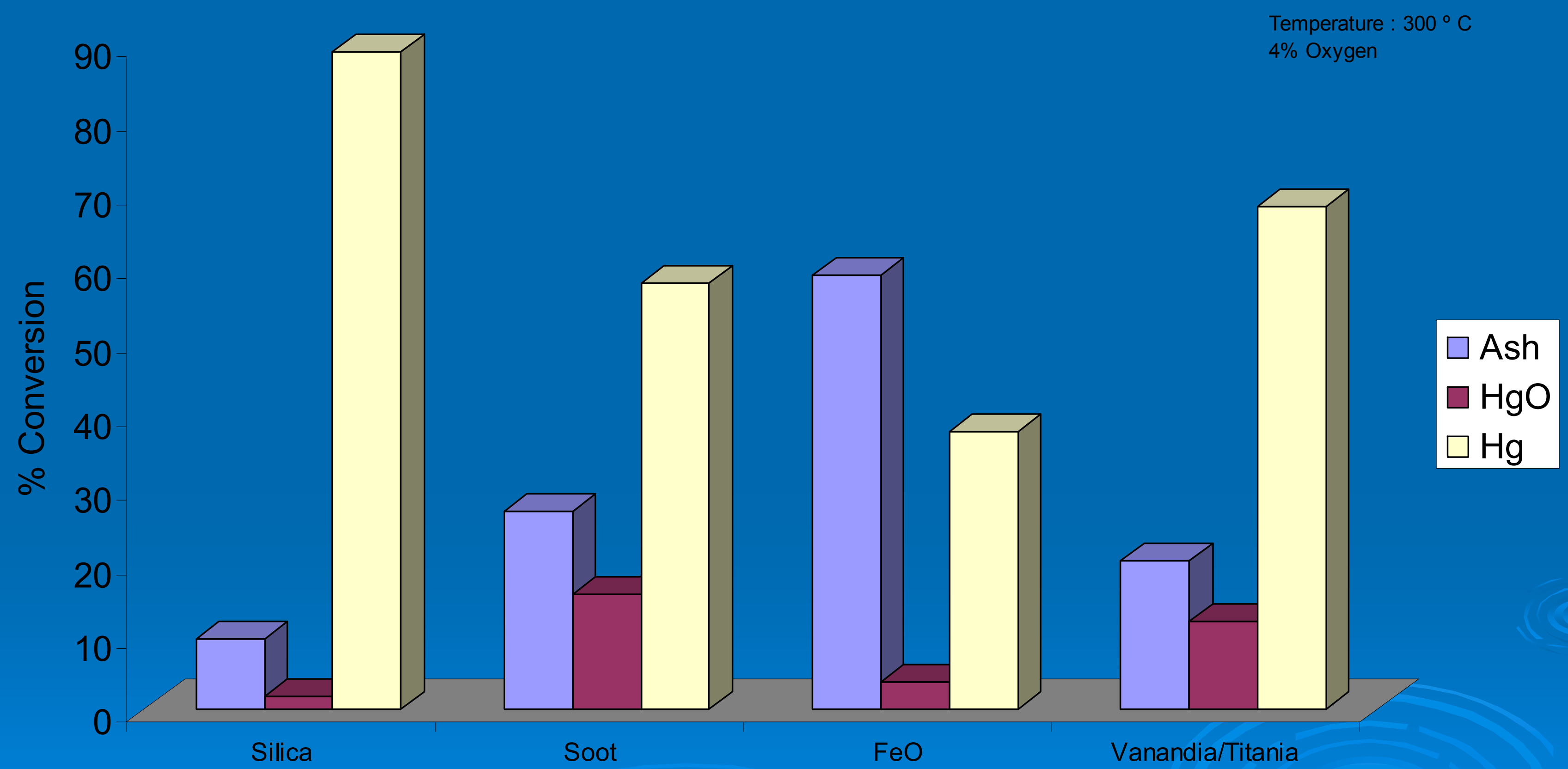




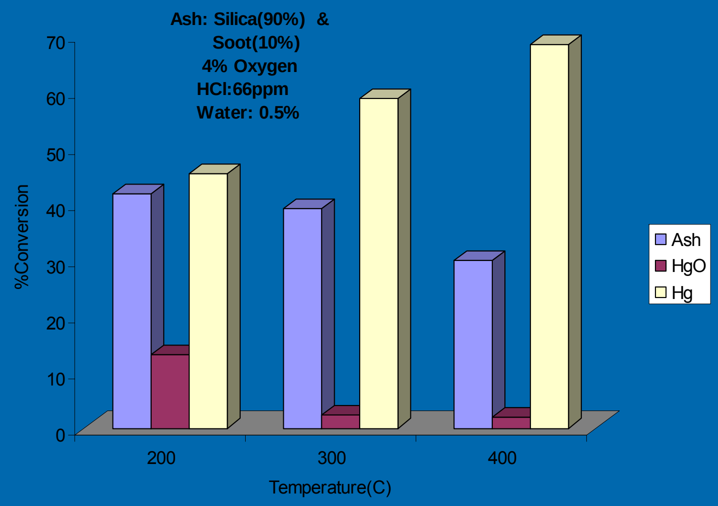
Surface Catalyzed Transformation: Presence of Water and HCl

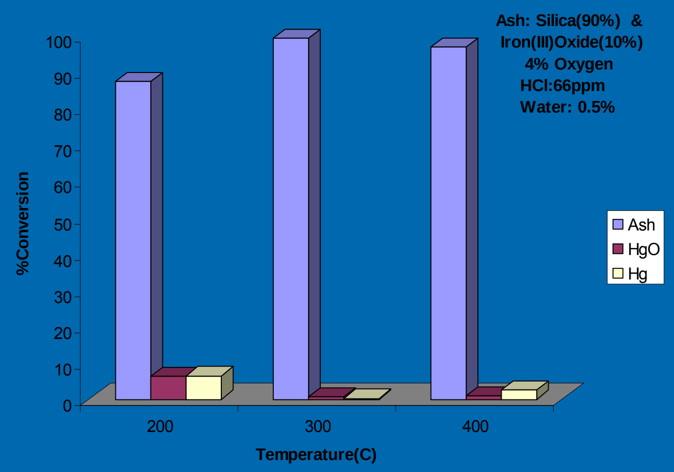


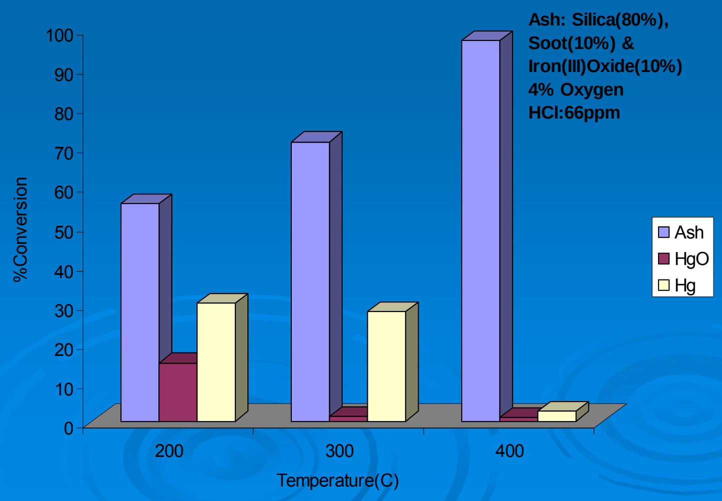
Mercury Oxidation on Model Fly Ashes



Surface Catalyzed Transformations : Presence of HCl







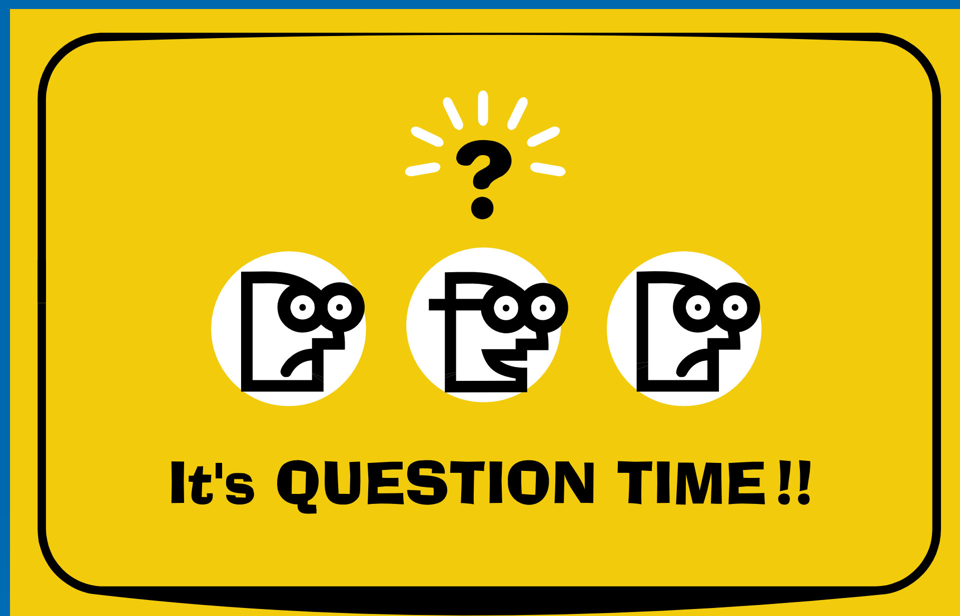
Conclusions

- Desorption modifies the ash and also removes most of the extractable carbon
- Soot shows low adsorbtion and high oxidation capabilities and hence may be responsible for the oxidation properties of fly ash.
- Iron Oxide seems to be a good adsorber of mercury.
- Addition of HCl seems to increase mercury oxidation and inhibits mercury adsorption.
- Under the post-combustion zone conditions HCl is a slightly better oxidizing agent than HBr

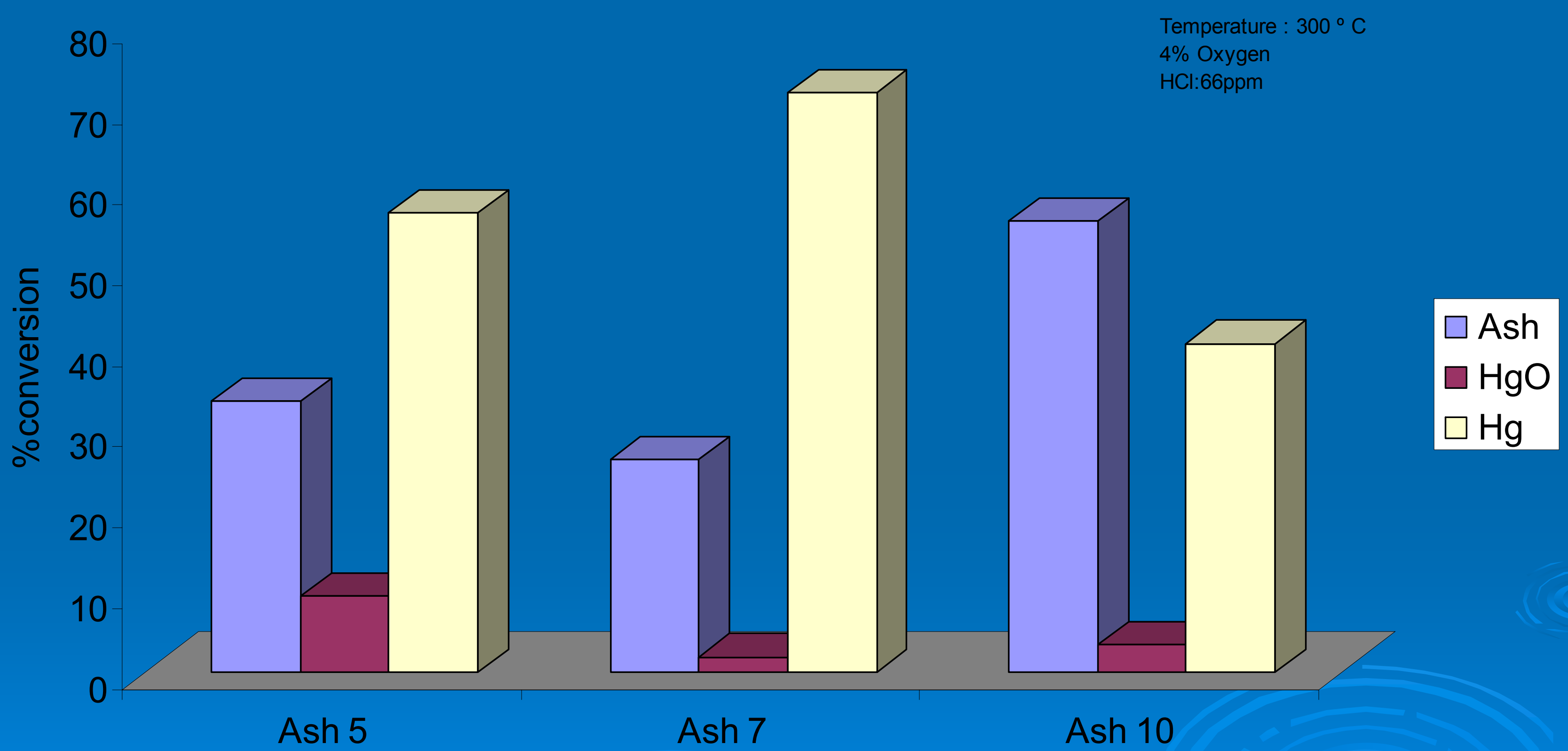
Acknowledgement

This work is partially supported by DoE grant (DE-PS26-05NT42472) and Ohio Coal Development Office.

Questions



Mercury Chlorination (same plant)



Data Analysis and Modeling

$Hg^{0}(g) + X(g)\ (Cl_2 \text{ or } O_2) \rightarrow Hg^{+2}X(g)$

$Hg^{0}(s) + X(g)\ (Cl_2 \text{ or } O_2) \rightarrow Hg^{+2}X(s)$

$Hg^{0}(g) + X(s)\ (Cl \text{ or } O) \rightarrow Hg^{+2}X(s)$

$Hg^{0}(s) + X(s)\ (Cl \text{ or } O) \leftrightarrow Hg^{+2}X(s)$

$Hg^{+2}X(s) \rightarrow Hg^{+2}X(g)$

$Hg^{+2}X(s) + R(g)\ (SO_2 \text{ or } CO) \rightarrow Hg^{0}(s) + RO(g)$

$Hg^{0}(s) \leftrightarrow Hg^{0}(g)$

$Hg^{+2}X(g) + R(g)\ (SO_2 \text{ or } CO) \rightarrow Hg^{0}(g) + RO(g)$

Background

- Gas-phase equilibrium assumption is not valid for mercury containing species at Temp < 500ºC.
- Post combustion zone temperatures range from 700ºC to ambient and the gas residence times are in the range of 2 to 10 seconds.
- Gas quench and surface catalyzed reactions (cool zone reactions) should be important.
- The results of recent studies have clearly shown that presence of fly ash enhances mercury oxidation under post-combustion zone conditions.