## 2012 台灣氧氣使用安全研討會 Oxygen Safety Seminar 2012 Taiwan





## **Oxygen Safety in ASU Design**

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Vice President

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## **Bill Pearce**

Bill Pearce is currently based in Shanghai, China and is Vice President for On-site Business Development and Merchant Product Sales for Praxair in Asia.

Bill has held a variety of positions with Praxair over the last 27 years in sales, engineering, and business management. Since arriving in Shanghai in 2010, Bill has supported the Asia country business teams in new on-site business acquisition, development of competitive supply systems, and new business strategies to sell merchant products.

A 1982 graduate of the Drexel University in Chemical Engineering with an MBA from Tulane University.



#### MURDOCH HACKGATE MESS CASTS I SHADOW OVER CAMERON GOVT

#### 16 die in Vizag Steel Plant blast

**GM** Too Killed **During Trial Of** Oxygen Unit

TIMES NEWS NETWORK

Visakhapatnam: in the worst-ever accident in the history of Viskhapatnass Staal Plant (VSP), 16 people acluding general mi Tragedy unprecedented: P7

Kaisi Naik, were hurnt alive following a buge explosion in the recently commissioned oxygen plant in the steel metting shop II unit on Wedn, why night. Fifteen run of the recently commis-workers were seriously in aloned exysten plant Most of the dealth full may the victims were contract workers jured and

One of the injuried at a hospital in Visua The blast took place at workers. At the time of the around 8.45pm when the offi-



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swept through the unit. All the workers and offi-clais present in the oxygen

plant were charred to death. The injured suffered 80%-

90% harris and wars taken to aven Hills Hospital Gajuwaka MLA Venitata

unalah confirmed to TOI

that 16 workers had died in the mishap. The steel plan

management were not avail-

able for commant even a cou

nip of hours after the acci-

dant. Trade union leaders

allege that maintenance

works in the plant had been neglected for more than a

The new SMS II wing,

#### 14 burnt alive in **explosion** at VSP

DC CORRESPONDENT

In the biggest actident till date at the Visichiapathum Steel Plant, at least 14 per-sons died and 11 were criti-cally injured when the coy-gan plant in the Steel Neet Ship-II exploded on Worksaday night.

Wormsaday night. Sources said that workers and field setting exacutives were citecting for leads in the converter bell when the accident tool place. The new converter aupolt ing corporation SMS-II was on a trial run as part of VSP's methods are reserved. ambitious expansion plans. At least three among the dead were in managerial posts and some were from a private construction com-puny. Around three dead bodies were sont to the stoel plant mortuary and staff were trying to retrieve the other bodies from the spot. The severaly injured were rushed to the Steel Plant

a mistake on the part of the VSP management which General Hespital and other earby corporate hospitals, where their condition is was in a hurry to commisdd to be critical. sion projects as part of "We four that more than expansion plan. said to be critical

13 persons died on the spot and around four received more than do per cent bu-On May 22, a conveyor belt in Blast Purnace-III, carrying raw material had rns," said Goluwaka MLA completely melted in the surfy morning hours as a result of which the entire Ch. Venkata Ramalah. Intur leader Gandham Venkat Rao said that it was



Troduction had come in a standstill. It host also enued losses of about 21 crore. However, there had been no crossili-tios then.

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Turlia- 22 Sold!



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## Outline

- Goal
- Main condenser safety basics
- Factors impacting safety & design
- Main condenser design considerations
- Early period Main condenser failures
- Learnings and condenser advancements
- Summary



## **Goal of this Presentation**

- Trace the evolution of main condenser safety and its influence on operation and design
- Capture important lessons learned
- Create a knowledge framework for the safe operation of air separation units



## Main Condenser/Reboilers

- At the heart of cryogenic air separation plant safety
- Contaminants that reach the distillation columns concentrate in the liquid oxygen stream that is vaporized in the main condenser.
- Main condenser design and operation significantly influence whether or not the contaminants can introduce a safety risk



## Main Condenser Safety - Basics

#### Risk Triangle - Eliminate ANY one of 3 ingredients and there is NO reaction

- Oxidizer (Oxygen)
  - Unavoidably present In reboiler-condensers of ASUs
- Ignition Starter
  - Cannot eliminate all ignition mechanisms
- Fuel
  - Sufficient fuel (contaminant hydrocarbons HCs) is available in feed air to ASUs, which if allowed can concentrate to LEL
  - HCs (hydrocarbons) should not be allowed to reach the following limits at any location in the ASU
    - The LEL
    - Concentration which forms a solid
    - Concentration that forms a second liquid phase



## Main Condenser – Factors that Influence Safety

- Contaminants in air
- Performance of air purification step, use of LOX absorbers
- Magnitude of contaminants enrichment in LOX entering the main condenser
- Main condenser design and operation



## **Contaminants in Ambient Air**

- An important factor in the design and operation
- Three types
  - corrosive: acid gases, sulfur oxides, ammonia
  - plugging: H2O, CO2, N2O, particulates (filterable, solids, aerosols)
  - flammable: Hydrocarbons
- Plugging and flammable components directly affect safety
- Little control over air quality and difficult to measure
- Periodically monitor for unusual changes in air quality



## Air purification System

- Significant factor in main condenser and air separation plant safety
- Purification system evolution strongly linked to type of main heat exchangers employed.
- Purification system with varied levels of hydrocarbon (HC) removal impacts HC build-up and safety risks



## **Air purification (Earlier Plants)**





### Air purification System Earlier Plants

- Earlier plants used regenerators for main heat exchange that also removed moisture and CO2 from air, and a device to trap solid CO2 and ice.
- Removal of hydrocarbons and other impurities achieved by gas-phase or liquid-phase gel-traps (CEGT)
- Gel traps did not remove all the hydrocarbons. Recirculation Gel Traps (RGT) near the MC was also added to offer additional protection - guard adsorbers/LOX filters.
- Regenerators were subsequently replaced by reversing heat exchangers that adopted the same air purification methods as above.
- Addition of halocarbon R-13 was used to suppress boiling/concentrating of contaminant rich liquid solution in the main condenser.



## Air purification System Current Practice

- Molecular sieve (adsorbent) based purifiers ahead of primary heat exchanger (PHX) – prepurifiers/front-end purifiers
- Extremely efficient contaminant removal system water, acetylene & C4+ HC





## **Technology Timeline Air purification & Cooling**





## Process Dependent Enrichment of Contaminants in LOX Stream

- High boiling contaminants that enter the distillation columns (through air) tend to concentrate in the liquid Oxygen stream
- Concentration or accumulation of contaminants in the LOX stream depends on the process cycle (GOX from column or LOX pumped cycle)
- GOX cycles require purge to limit contaminant accumulation from unsafe levels in the main condenser sump



## **Process Dependent Enrichment of Contaminants in LOX Stream**

| Contaminants | Concentration<br>in air | Concentration at prepurifier exit | Concentration in<br>LOX in MC sump<br>(with 2% * O2 purge) | Concentration in<br>LOX in MC sump<br>(LOX pumped cycle) |
|--------------|-------------------------|-----------------------------------|--|--|
| тнс          |                         |                                   | <300 ppm   | <30 ppm  |
| CO2          | ~425 ppm                | <0.1 ppm                          | <4 ppm   | <400 ppb   |
| N2O          | ~350 ppb                | ~150 ppb                          | 7.5 ppm  | 750 ppb  |

\* 2% of air flow into the column



## Main Condenser Design and Operation

#### Types of main condensers

- Plate-fin brazed aluminum heat exchanger
- Textured surface plate-fin heat exchanger
- Highflux main condenser

#### Operation

- Recirculating thermosyphons
- Recirculating downflow
- Once-through downflow



# Main Condenser Technology Timeline – Praxair Practice





## Main Condenser Early period Experience

- Three Reboiler-Condenser Explosions in the Early 1960s
  - 1960 Belle, WV Plant 1
    - Destroyed reboiler-condenser, damaged high and low pressure columns
  - 1963 Cleveland, OHIO
    - Major damage to heat exchangers, minor damage to surrounding equipment
  - 1964 Belle, WV Plant 2
    - Extensive plant damage

No serious injuries incurred in any of these cases



# Typical Main Condenser Core Damage Cleveland, OHIO





## **Praxair Response**

#### Investigation

- ~450 TPD plants RHX (reversing heat exchanger)
- Main reboiler-condensers utilizing 17"x21"x90" BAHX cores 14 FPI, no alignment, non-gapped
- No evidence of unusual atmospheric contamination
- Normal HC concentrations in sumps
- Ignition mechanisms could not be determined
- Belle 1 Boiling to dryness
  - Inadequate Operating Level
- Cleveland Dead-ended boiling
  - Plugged Passages perlite & water ice
- Belle 2 Dead-ended boiling
  - Plugged Passages
  - Most Reboiler/ Condenser cores were undamaged!



### Praxair Response Praxair Fundamentals

- Considerable effort theoretical and laboratory Investigations
- Measurement and correlation of fundamental thermodynamic and flammability Data
- Improved understanding of contaminant behavior
- Tests involving conditions that would plug exchangers
  - Exchanger flow area a key variable
  - Frozen contaminants
  - Permanent solids
- Development of new types of heat exchangers.



## Praxair Response

#### Changes

#### Revisions to Operating Practice

- Increased Liquid levels in reboiler-condensers
- Increased Recirculation Gel Trap flow & thaw frequency
- Cold End Gel Trap installation & thaw
- Fluorocarbon addition

#### Design of Reboilers-Condensers

- BAHX
  - Type of fins
  - Alignment & gapping
- New designs
  - Textured Surface (TS) cores (BAHX with no fin in LOX passages)
  - HighFlux Main Condensers
    - Relatively large flow area
    - Thicker material
    - Promoted ignition tests No cases of Aluminum participation in reaction



## Highflux Tube Performance Promoted Ignition Tests



#### **Highflux tube with promoter – pre ignition tests**



Test 7, Tube 11, 300psig LOX, static, 0.05g/cm2 promoter, 96% promoter consumed

#### **Highflux tube – post ignition tests**



#### Praxair Main Condenser Highflux Design Praxair



## Highflux Exchanger Enhancements

- Large oxygen flow passage clearance
  - Tube ID 16 mm vs. 1.5 mm in BAHX
- Higher tube thickness
  - Tube thickness 2.5 mm vs. 0.4 mm fin thickness
- Failures, if any, would be isolated to individual tubes and contained by the nitrogen atmosphere surrounding it.
- Less flow resistance very tolerant of lower liquid levels and still have no boiling to drynes
- More than 30 years of operating experience



## Main Condenser Design Recent Developments

- BAHX downflow technology Praxair's practices
- Designed for high recirculation rates to ensure complete wetting on boiling surface, and requires recirculation pump.
- LOX pumped cycles and Molecular sieve prepurifier is a prerequisite
- Requires a 3-year thaw period.



## Summary

- Over the past 4 to 5 decades, performance and safety of main condensers were concurrently improved through:
  - Better identification of risk factors
  - Significant improvements in air purification technology
  - Significant improvements in condenser-reboiler technology
  - Better operation through monitoring and appropriate safeguards
- CGA Publications P-8\* "Safe Practices Guide for Cryogenic Air Separation Plants" and P-8.4\*\* "Safe Operation of Reboiler/Condensers in Air Separation Units – EIGA 65/06 covers these learnings.

\*AIGA 056/08, \*\* AIGA 035/06 are equivalent publications



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