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

行政院勞工委員會

台灣區高壓氣體
工業同業公會

Asia Industrial
Gases Association

國立臺北科技大學

# Oxygen Safety in ASU Design

# 空分廠的氧氣安全設計

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# Bill Pearce
## 比爾皮爾斯

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.

比爾皮爾斯現任職於普萊克斯中國上海副總裁，負責亞洲大宗氣體事業發展與液態大宗氣體產品銷售。

比爾在過去**27**年中，在普萊克斯不同部門擔任過多個職務，包括銷售、工程及業務管理。 自從**2010**年到上海以來，比爾協助亞洲業務團隊拓展了新現場製氣業務，發展具競爭力的供應系統，並制定了液態大宗氣體銷售策略。

比爾**1982**年畢業於卓克索大學化學工程系並獲得杜蘭大學工商管理碩士

MURDOCH HACKGATE MESS CASTS ITS SHADOW OVER CAMERON GOVT | 14

# 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 Visakhapatnam Steel Plant (VSP), 16 people, including general manager Kalsi Naik, were burnt alive following a huge explosion in the recently commissioned oxygen plant in the steel melting shop II unit on Wednesday night. Fifteen workers were seriously injured and the death toll may ... group, sources said.

▸ Tragedy unprecedented: P7

One of the injured at a hospital in Vizag

The blast took place at around 8.45pm when the officials were conducting a trial run of the recently commissioned oxygen plant. Most of the victims were contract workers. At the time of the blast, at least 31 workers, including GM and DGM-rank officials, were on duty.

After the massive blast, a huge fire raged across the plant. The oxygen plant was completely gutted as flames swept through the unit.

All the workers and officials present in the oxygen plant were charred to death. The injured suffered 80%-90% burns and were taken to Seven Hills Hospital.

Gajuwaka MLA Venkataramaiah confirmed to TOI that 16 workers had died in the mishap. The steel plant management were not available for comment even a couple of hours after the accident. Trade union leaders allege that maintenance works in the plant had been neglected for more than a year.

The new SMS II wing, which was constructed as part of the expansion works of the plant, was commissioned recently.

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# 14 burnt alive in explosion at VSP

DC CORRESPONDENT
VISAKHAPATNAM, JUNE 13

In the biggest accident till date at the Visakhapatnam Steel Plant, at least 14 persons died and 11 were critically injured when the oxygen plant in the Steel Melt Shop-II exploded on Wednesday night.

Sources said that workers and two senior executives were checking for leaks in the converter belt when the accident took place. The new converter supplying oxygen to SMS-II was on a trial run as part of VSP's ambitious expansion plans.

At least three among the dead were in managerial posts and some were from a private construction company. Around three dead bodies were sent to the steel plant mortuary and staff were trying to retrieve the other bodies from the spot.

The severely injured were rushed to the Steel Plant General Hospital and other nearby corporate hospitals, where their condition is said to be critical.

"We fear that more than 12 persons died on the spot and around four received more than 80 per cent burns," said Gajuwaka MLA Ch. Venkata Ramaiah.

Intuc leader Gandham Venkat Rao said that it was a mistake on the part of the VSP management which was in a hurry to commission projects as part of expansion plan.

On May 22, a conveyor belt in Blast Furnace-III, carrying raw material had completely melted in the early morning hours as a result of which the entire production had come to a standstill.

It had also caused losses of about ₹1 crore. However, there had been no casualties then.

Relatives of VSP blast victims cry inconsolably at the hospital. — DECCAN CHRONICLE



మృతులలో జీఎం, ముగ్గురు డీజీఎంలు!

ఆక్సిజన్

10 మంది దుర్మర

ఆరుగురు గల్లంతు.. 9 మందికి గా

# Outline 綱要

- Goal 目的
- Main condenser safety basics 主冷凝器安全基本原則
- Factors impacting safety & design 影響安全與設計的因素
- Main condenser design considerations 主冷凝器設計考量
- Early period – Main condenser failures 早期主冷凝器失效探討
- Learnings and condenser advancements 學得經驗與冷凝器進展
- Summary 總結

# Goal of this Presentation 本演講目的

- Trace the evolution of main condenser safety and its influence on operation and design

  主冷凝器在安全性的演變進化及其對操作與設計的影響

- Capture important lessons learned

  獲得重要學習的教訓

- Create a  knowledge framework for the safe operation of air separation units

  建立對空分廠的安全操作知識

# Main Condenser/Reboilers 主冷凝器與再沸器

- At the heart of cryogenic air separation plant safety

  低溫空分廠安全的核心

- Contaminants that reach the distillation columns concentrate in the liquid oxygen stream that is vaporized in the main condenser.

  進入蒸餾塔系統的污染物會集中在液氧流中, 此液氧流會在主冷凝器被蒸發

- Main condenser design and operation significantly influence whether or not the contaminants can introduce a safety risk

  主冷凝器設計與操作將顯著地影響污染物是否會導致安全風險

# Main Condenser Safety - Basics主冷凝器安全 – 基本原則

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

  危險三要角-移除三個成份任一個將不會有反應

  – Oxidizer (Oxygen) 氧化物(氧氣)
    - Unavoidably present In reboiler-condensers of ASUs

      無可避免出現在空分廠的再沸器-冷凝器
  – Ignition Starter 火源
    - Cannot eliminate all ignition mechanisms 無法移除所有引火機械裝置
  – Fuel 燃料
    - Sufficient fuel (contaminant hydrocarbons – HCs) is available in feed air to ASUs, which if allowed can concentrate to LEL

      當進入空分廠中燃料(碳氫污染物)聚集數量達到燃燒下限量
    - **HCs (hydrocarbons) should not be allowed to reach the following limits at any location in the ASU** 一碳氫化合物在空分廠任一位置,不應容許到達下列狀況
      - The LEL 燃燒下限
      - Concentration which forms a solid 聚集形成一固體
      - Concentration that forms a second liquid phase 聚集形成一個二次液相

# Main Condenser – Factors that Influence Safety
# 主冷凝器 – 影響安全的因素

- **Contaminants in air**

  空氣中的污染物

- **Performance of air purification step, use of LOX absorbers**

  空氣純化步驟的效果, 使用液氧吸附器

- **Magnitude of contaminants enrichment in LOX entering the main condenser**

  存在於液氧中之高風險污染物進入主冷凝器時的程度

- **Main condenser design and operation**

  主冷凝器的設計與操作

# Contaminants in Ambient Air 週遭空氣中的污染物

- **An important factor in the design and operation**
  是設計與操作安全的重要因素
- **Three types** 汙染物有下列三種類型
  - corrosive: acid gases, sulfur oxides, ammonia
    腐蝕性的： 例如酸性氣體, 氧化硫, 氨
  - plugging: $H_2O$, $CO_2$, $N_2O$, particulates (filterable, solids, aerosols)
    堵塞性的：例如水份, 二氧化碳, 笑氣, 微塵粒子(可過濾的, 固體, 氣凝膠)
  - flammable: Hydrocarbons 可燃性的： 例如碳氫化合物
- **Plugging and flammable components directly affect safety**
  堵塞及可燃性的成分將可直接影安全
- **Little control over air quality and difficult to measure**
  空氣品質幾乎不可控制並且難以量測
- **Periodically monitor for unusual changes in air quality**
  定期監控空氣品質中不尋常的改變

# Air purification System 空氣純化系統

- **Significant factor in main condenser and air separation plant safety**

  對主冷凝器及空分廠的安全而言是一個重要因素

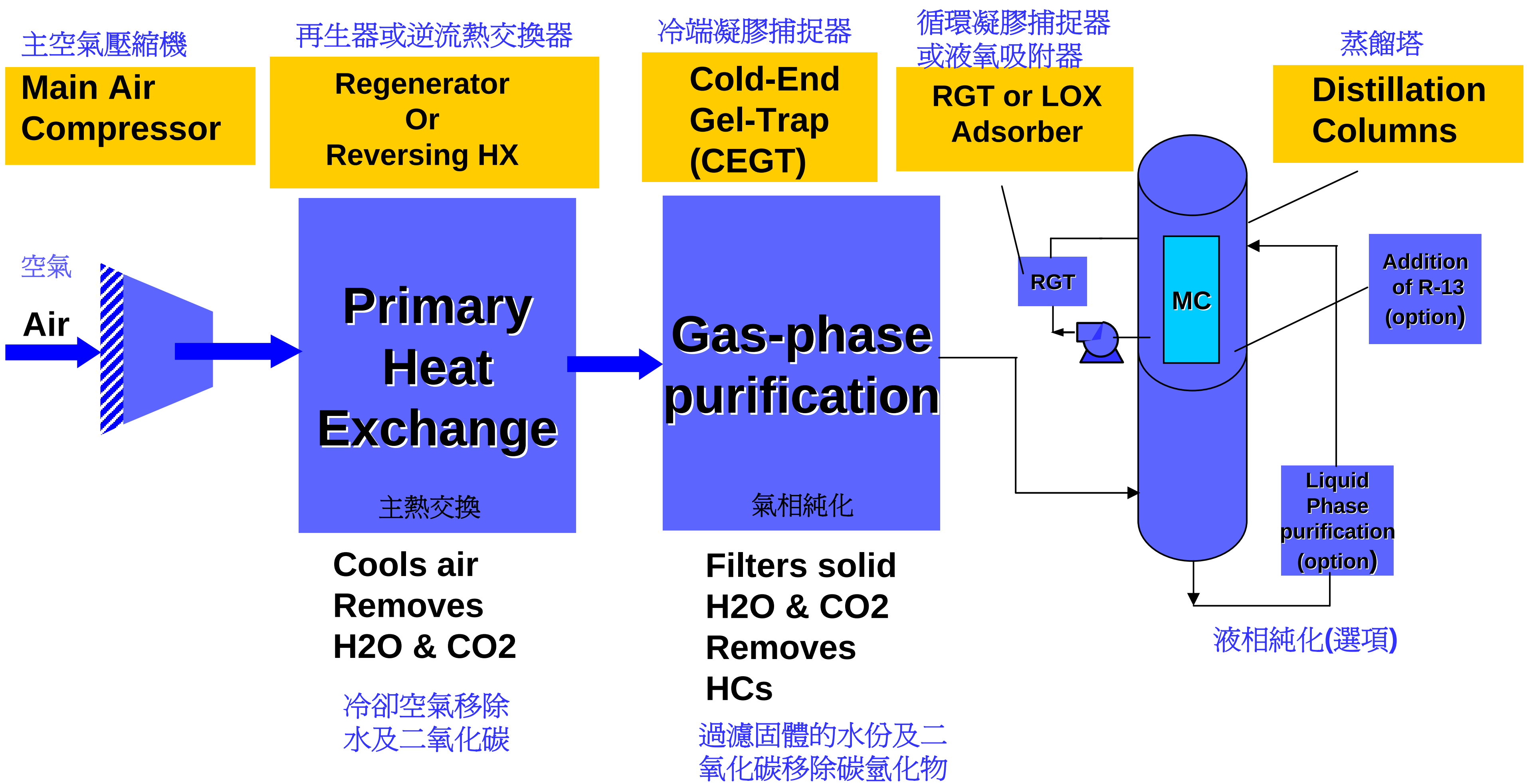
- **Purification system evolution strongly linked to type of main heat exchangers employed.**

  純化系統的進化與所使用的主熱交換機有直接地關聯

- **Purification system with varied levels of hydrocarbon (HC) removal impacts HC build-up and safety risks**

  不同等級的去除碳氫化物純化系統會影響到碳氫化合物的積聚與工廠運行安全風險

# Air purification (Earlier Plants) 空氣純化(早期工廠)



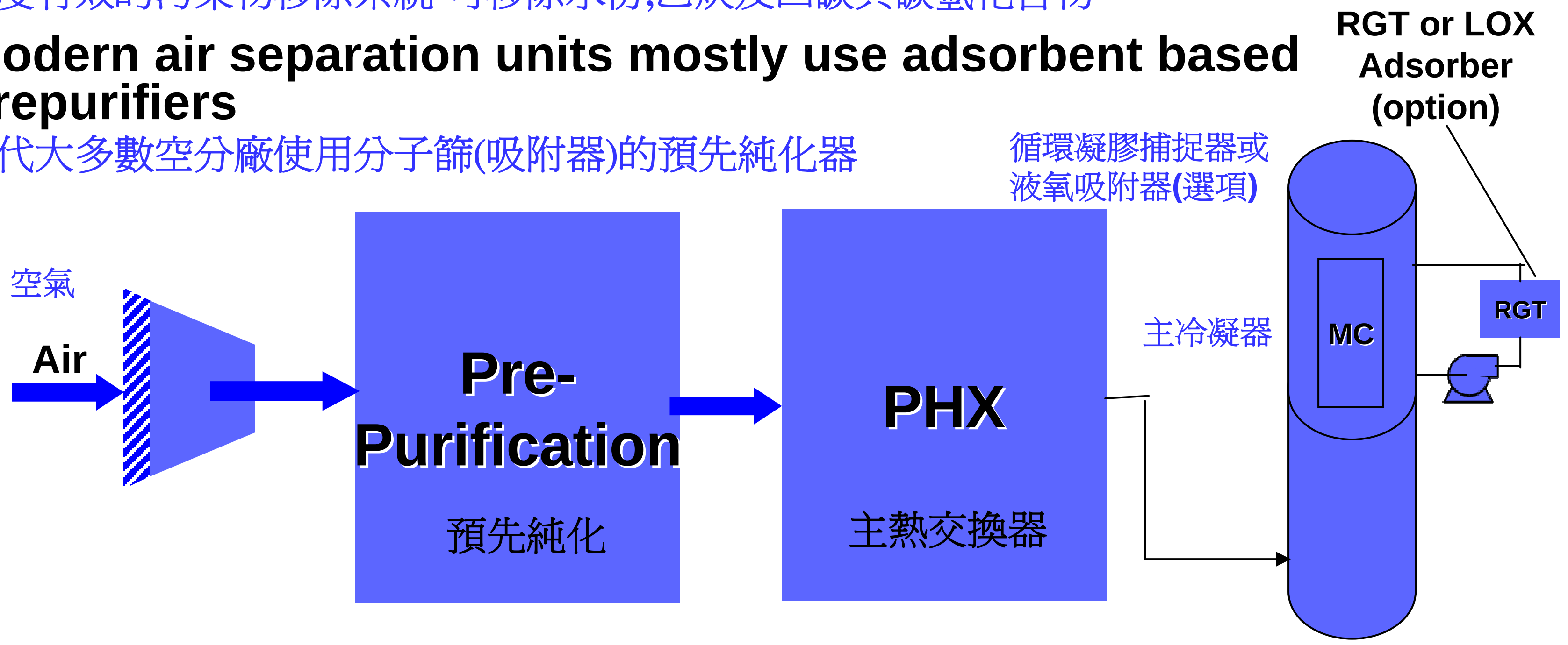
# Air purification System 空氣純化系統

## Earlier Plants 早期工廠

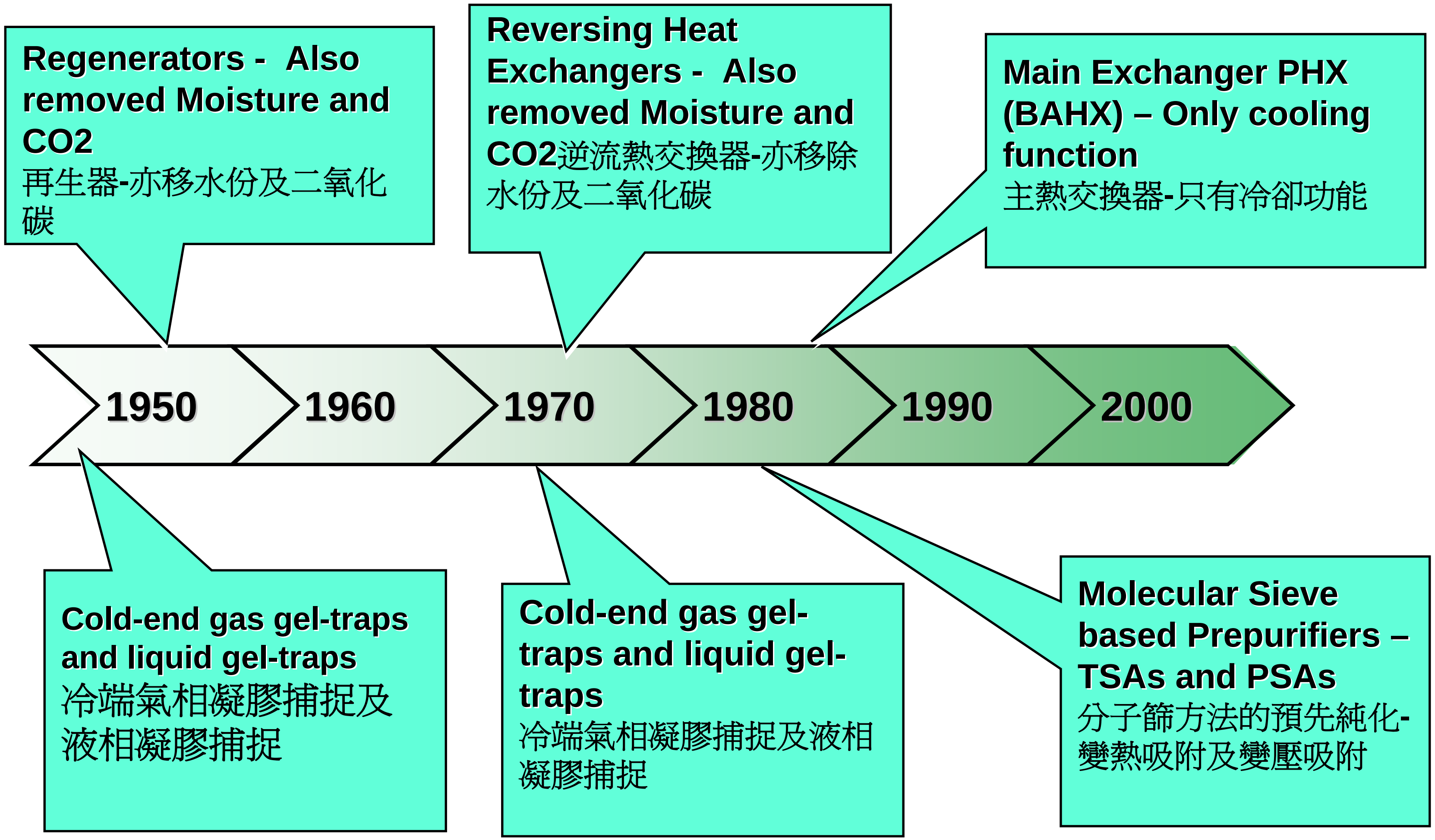
- **Earlier plants used regenerators for main heat exchange that also removed moisture and $CO_2$ from air, and a device to trap solid $CO_2$ and ice.**
  早期工廠給主熱交換器使用之純化再生器可自空氣移除水份及二氧化碳, 並有一個裝置用來捕捉固態二氧化碳與冰
- **Removal of hydrocarbons and other impurities achieved by gas-phase or liquid-phase gel-traps (CEGT)**
  藉由氣相或液相凝膠捕捉器將碳氫化物及其他不純物移除
- **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.**
  凝膠捕捉器不能將所有碳氫化物移除;靠近主冷凝器的再循環凝膠捕捉器也增加提供額外防護-吸附器/液氧過濾器
- **Regenerators were subsequently replaced by reversing heat exchangers that adopted the same air purification methods as above.**
  再生器隨後被逆流熱交熱換器取代, 它採用上述相同的空氣純化方法
- **Addition of halocarbon R-13 was used to suppress boiling/concentrating of contaminant rich liquid solution in the main condenser.**
  鹵烴族R-13添加用來抑制在主冷凝器中富含污染物液体的沸騰/積聚

# Air purification System 空氣純化系統
# Current Practice 現行方法

- **Molecular sieve (adsorbent) based purifiers ahead of primary heat exchanger (PHX) – prepurifiers/front-end purifiers**
  分子篩(吸附器)構成的純化器置於主要熱交換器之前
- **Extremely efficient contaminant removal system – water, acetylene & C4+ HC**
  極度有效的污染物移除系統-可移除水份,乙炔及四碳與碳氫化合物
- **Modern air separation units mostly use adsorbent based prepurifiers**
  現代大多數空分廠使用分子篩(吸附器)的預先純化器



# Technology Timeline 技術時間軸
# Air purification & Cooling 空氣純化及冷卻



# Process Dependent Enrichment of Contaminants in LOX Stream

## 製程依賴的液氧流中污染物

- **High boiling contaminants that enter the distillation columns (through air) tend to concentrate in the liquid Oxygen stream**
  經由空氣進入蒸餾塔的高沸點污染物易於在液氧流中聚集
- **Concentration or accumulation of contaminants in the LOX stream depends on the process cycle (GOX from column or LOX pumped cycle)**
  在液氧流中污染物聚集的或累積依製程循環而定(氣氧來自蒸餾塔或液氧抽取循環)
- **GOX cycles require purge to limit contaminant accumulation from unsafe levels in the main condenser sump**
  氣氧循環需要做沖吹處理將自不安全等級累積之污染物限制在可接受的範圍於主冷凝器中

# Process Dependent Enrichment of Contaminants in LOX Stream

## 製程所需之液氧流中污染物規格設定

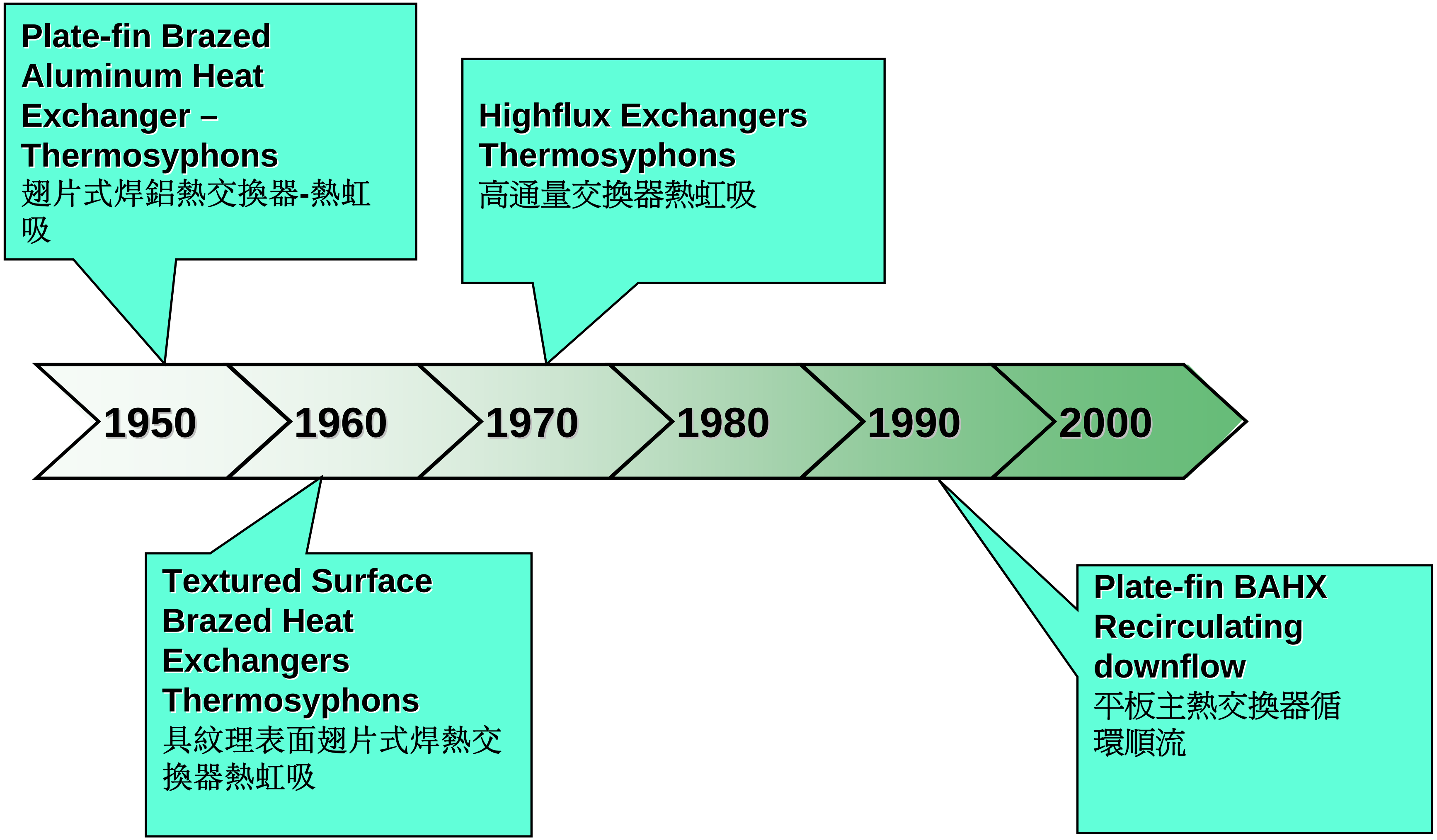
| Contaminants<br>污染物 | Concentration in air<br>空氣中濃度 | Concentration at prepurifier exit<br>在預純化器出口濃度 | Concentration in LOX in MC sump (with 2% * O2 purge)<br>在主冷凝器液氧流中的濃度(以2%氧氣沖吹) | Concentration in LOX in MC sump (LOX pumped cycle)<br>在主冷凝器中的液氧流的濃度(液氧抽取循環) |
|---|---|---|---|---|
| THC<br>總碳氫化合物 | | | <300 ppm | <30 ppm |
| CO2<br>二氧化碳 | ~425 ppm | <0.1 ppm | <4 ppm | <400 ppb |
| N2O<br>笑氣 | ~350 ppb | ~150 ppb | 7.5 ppm | 750 ppb |

* 2% of air flow into the column
2%的空氣流入蒸餾

# Main Condenser Design and Operation
# 主冷凝器設計與操作

- **Types of main condensers** 主冷凝器類型
  - – Plate-fin brazed aluminum heat exchanger 翅片式銲鋁熱交換器
  - – Textured surface plate-fin heat exchanger
    具紋理表面的翅片式熱交換器
  - – Highflux main condenser 高通量主冷凝器
- **Operation** 操作
  - – Recirculating thermosyphons 循環熱虹吸
  - – Recirculating downflow 循環順流
  - – Once-through downflow 單程順流

# Main Condenser Technology Timeline – Praxair Practice 主冷凝技術時間軸-Praxair方法



# Main Condenser Early period Experience 主冷凝早期經驗

- **Three Reboiler-Condenser Explosions in the Early 1960s** 在60年代初期三個再沸器-冷凝器爆炸
  - 1960 Belle, WV Plant 1
    - Destroyed reboiler-condenser, damaged high and low pressure columns
      再沸器-冷凝器毀壞, 破壞高低壓蒸餾塔
  - 1963 Cleveland, OHIO
    - Major damage to heat exchangers, minor damage to surrounding equipment
      熱交換器損壞較嚴重, 週遭設備輕微毀損
  - 1964 Belle, WV Plant 2
    - Extensive plant damage
      大規模工廠損壞

**No serious injuries incurred in any of these cases**
沒有導致嚴重傷害在任何這些案例

# Typical Main Condenser Core Damage Cleveland, OHIO

## 典型主冷凝器核心損壞, 克里夫蘭, 俄亥俄州

# Praxair Response Praxair 的因應

## Investigation 調查

- **~450 TPD plants – RHX (reversing heat exchanger)**
  工廠產氧量約每日450噸，逆流熱交換器
- **Main reboiler-condensers utilizing 17“x21”x90“ BAHX cores**
  **14 FPI, no alignment, non-gapped**
  主再沸器-冷凝器使用17”x21”90”主熱交換器核心翅片密度每英寸14个翅片, 無調校, 無縫隙
- **No evidence of unusual atmospheric contamination** 無證據表明大氣污染異常
- **Normal HC concentrations in sumps** 主冷釜中碳氫化合物濃度正常
- **Ignition mechanisms could not be determined** 點火機械不能判定
- **Belle 1 – Boiling to dryness** 貝爾案例1-沸騰至乾
  - Inadequate Operating Level 主冷操作液位不够
- **Cleveland - Dead-ended boiling** 克里夫蘭案例-死角沸騰
  - Plugged Passages – perlite & water ice 塞住的通道-珍珠岩及冰塊
- **Belle 2 - Dead-ended boiling** 貝爾案例2-死角沸騰
  - Plugged Passages 通道堵塞
  - Most Reboiler/ Condenser cores were undamaged!
    大部份再沸器/冷凝器核心未損壞

# Praxair Response Praxair 的因應

## Fundamentals 原理

- **Considerable effort - theoretical and laboratory Investigations**

  盡相當的努力-從理論與實驗室調查雙方面進行

- **Measurement and correlation of fundamental thermodynamic and flammability Data**

  測量並關聯基礎的熱力學及可燃性資料

- **Improved understanding of contaminant behavior**

  增進污染物行爲特性的了解

- **Tests involving conditions that would plug exchangers**

  包含會塞住交換器條件的測試

  - Exchanger flow area a key variable 交換器流動區域是一重要變數
  - Frozen contaminants 凍結的污染物
  - Permanent solids 永久的固體

- **Development of new types of heat exchangers.**

  新型熱交換器的開發

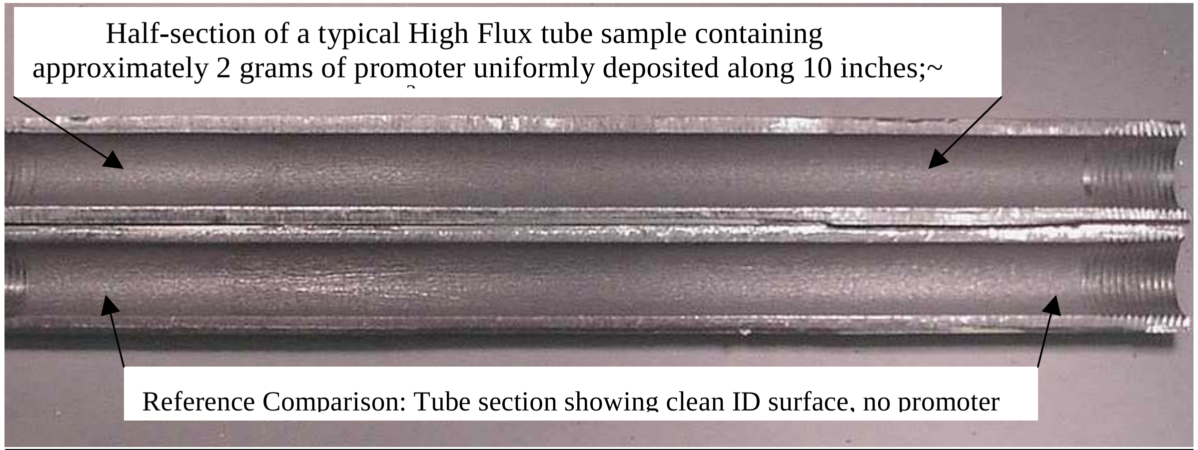
# Praxair Response Praxair的因應

## Changes 改變

- **Revisions to Operating Practice** 修訂操作方法
  - Increased Liquid levels in reboiler-condensers 增加再沸器-冷凝器液面高度
  - Increased Recirculation Gel Trap flow & thaw frequency 增加循環在凝膠捕捉流量及解凍頻率
  - Cold End Gel Trap installation & thaw 安裝冷端凝膠捕捉及解凍
  - Fluorocarbon addition 氟碳化合物添加
- **Design of Reboilers-Condensers** 再沸器-冷凝器的設計
  - BAHX 主熱交換器
    - Type of fins 翅片的類型
    - Alignment & gapping 校準與間隙
  - New designs 新設計
    - Textured Surface (TS) cores (BAHX with no fin in LOX passages) 紋理表面核心(主熱交換器無鰭在液氧通道)
    - HighFlux Main Condensers 高通量主冷凝器
      - Relatively large flow area 相對大流量區域
      - Thicker material 較厚的材料
      - Promoted ignition tests – No cases of Aluminum participation in reaction 升級的燃燒測試-沒有鋁參與反應的案例

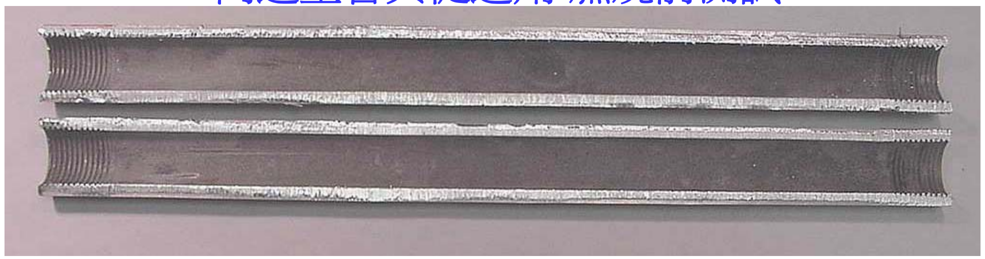
# Highflux Tube Performance 高通量管的性能

## Promoted Ignition Tests 促進的燃燒測試




## Highflux tube with promoter – pre ignition tests

高通量管與促進劑-燃燒前測試



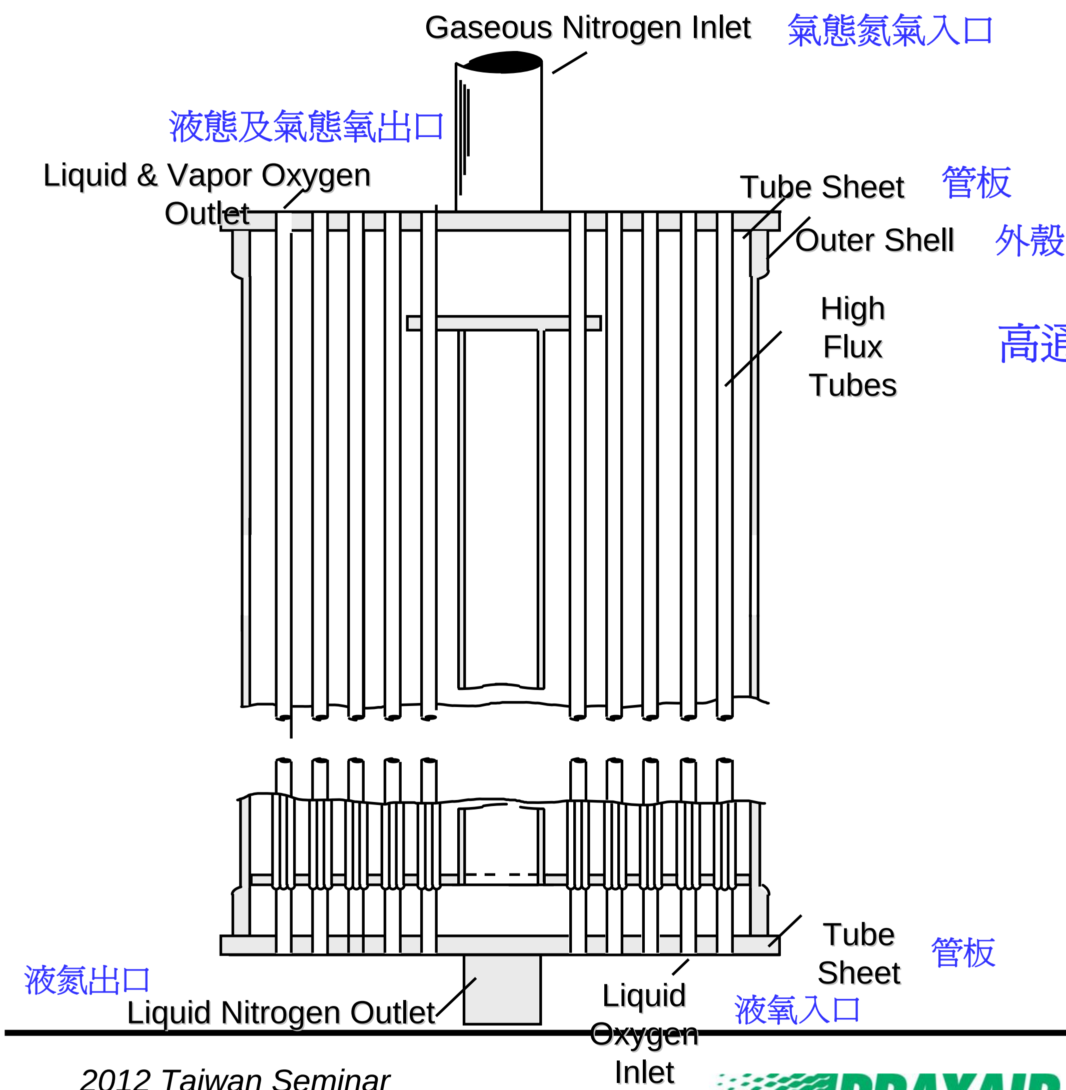
Test 7, Tube 11, 300psig LOX, static, 0.05g/cm2 promoter, 96%  promoter consumed

測試**7,** 管子**11, 300 psig**液氧**,**靜止的**, 0.05g/cm2**促進劑**, 96%**促進劑被消耗

## Highflux tube – post ignition tests 高通量管-燃燒後測試

# Praxair Main Condenser Highflux Design

## Praxair主凝器高通量設計




**Highflux Tube**

高通量管

# Highflux Exchanger Enhancements
## 高通量交換器提升

- **Large oxygen flow passage clearance** 大氣流量通道淨空
  - Tube ID 16 mm vs. 1.5 mm in BAHX 管內徑16mm對1.5mm在主熱交換器
- **Higher tube thickness** 較高的管厚度
  - Tube thickness 2.5 mm vs. 0.4 mm fin thickness

    管厚2.5mm對0.4mm鰭厚度
- **Failures, if any, would be isolated to individual tubes and contained by the nitrogen atmosphere surrounding it.**

  如有任何失效, 個別管路將與周圍環境中的氮氣隔離
- **Less flow resistance – very tolerant of lower liquid levels and still have no boiling to dryness**

  較小流量阻力-非常容忍較低的操作液位
- **More than 30 years of operating experience** 超過30年的操作經驗

# Main Condenser Design 主冷凝器設計
# Recent Developments 最新發展

- BAHX downflow technology – Praxair's practices

  主熱交換器順流技術-Praxair的設計

  – Designed for high recirculation rates to ensure complete wetting on boiling surface, and requires recirculation pump.

    以高循環率設計以確保完成沸騰表面的濕潤, 需要循環幫浦

  – LOX pumped cycles and Molecular sieve prepurifier is a prerequisite

    液氧抽取循環及分子篩預先純化器是必要條件

  – Requires a 3-year thaw period.

    每三年需要做一次解凍維修

# Summary 總結

- **Over the past 4 to 5 decades, performance and safety of main condensers were concurrently improved through:**
  在過去四十到五十年, 主冷凝器的性能與安全已同時由以下方式改進:
  - Better identification of risk factors 較佳的風險因子辨識
  - Significant improvements in air purification technology
    空氣純化技術的重大改進
  - Significant improvements in condenser-reboiler technology
    冷凝器-再沸器術技的重大改進
  - Better operation through monitoring and appropriate safeguards
    經由監控與適當的防護實現的較佳的操作
- **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.** 以上經驗可參考於壓縮氣體協會出版P-8低溫空分廠安全實務指南及P-8.4空分廠再沸器與冷凝器的安全操作-歐洲工業氣體協會文件65/06

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

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