Operation of an Ammonia Plant on a Start Up / Shut Down Cycle

Pan & Dimitri Orphanides

Today's Agenda

- Introduction
- Technical Characteristics
- Economical Considerations
- Lessons learned

PFI GREECE / Ammonia Unit

- ***PFI is the sole Fertilizer Producer in Greece***
- ***Two Production Facilities in Northern Greece, Thessaloniki and Kavala***
- ***Total Production capacity of 1.3 million tn/year. Covers over 45% of domestic market***
- ***Kavala Plant has the only Ammonia Unit in the country built in 1983-85 to use N.G. feed from associated oil /gas field in neighboring area***
- ***No Urea production in Greece***
- ***Pan Orphanides was PFI's Project director of this prototype high efficiency 400 MTD Ammonia plant***
- ***Dimitri Orphanides was Ammonia plant process Engineer during 2001 and 2002***

Ammonia Unit History

- *Plant conceived to exhaust small gas field at max. possible plant design capacity - energy efficiency, unprecedented in early 80ies for small capacity Ammonia units. General Contractor for EPC project KTI –Zoetermeer/Holland – today Technip*
- *Plant Start Up in 1985, nominal capacity of 400 MTD*
- *Plant ceased operation in 1994 due to exhaustion of field reserves and mothballed for long shut down.*
- *Plant resumed operation in 1997 after construction of N.G. pipeline connecting with imported Russian N.G.*
- *Plant was revamped in 1999 with capacity to 450 MTD*
- *Plant in turnaround in Nov. 2005 after 3 years continuous operation. Findings will be discussed*
- *Plant in normal operation until to date at 470 MTD*

Ammonia Plant Components

Main Sections	*Utility Sections*
•Hydrogen Production (KTI – Technip / DeS TSA/ UOP) Innovative application	• 9 MW Power Generation (AEG)
•Syngas Purification: PSA Unit (UOP) Innovative design	•Demin Water (Christ)
•Nitrogen Generator (Air Products & Atlas Copco)	•Ammonia Refirgeration (Stahl)
•Nitrogen /Syn. Gas Compressors (Nuovo Pignone reciprocating)	•Refrigerated Ammonia Storage Tank 10000 MT (UHDE)
•Casale Ammonia Synthesis Innovative design	• DCS /ESD (Foxboro /Hima)
• Process Gas Cooler Nuovo Pignone Innovative design	
• Synloop WHB Innovative design (Borsig)	

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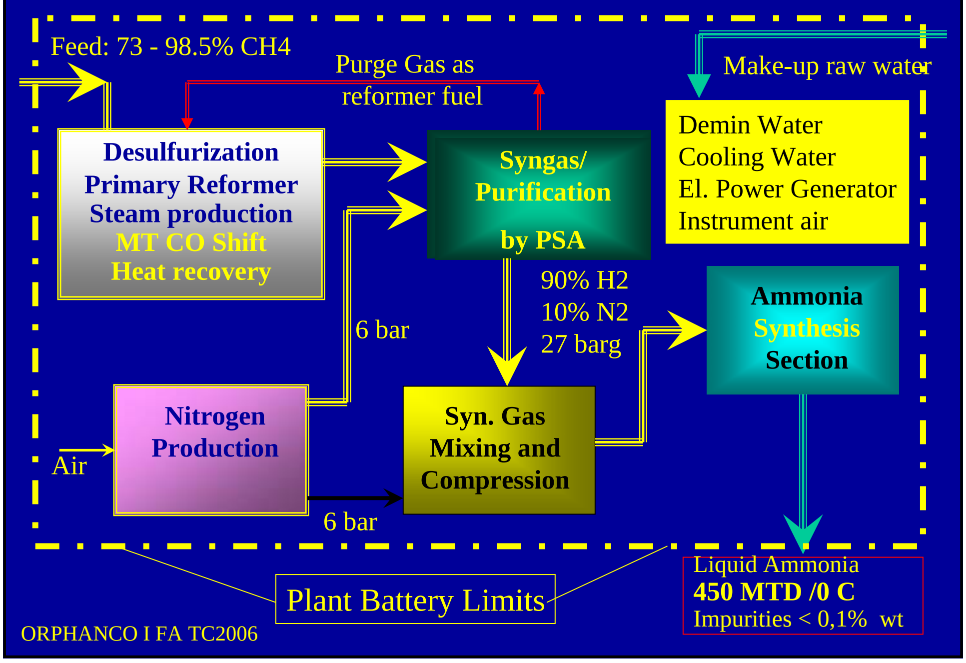
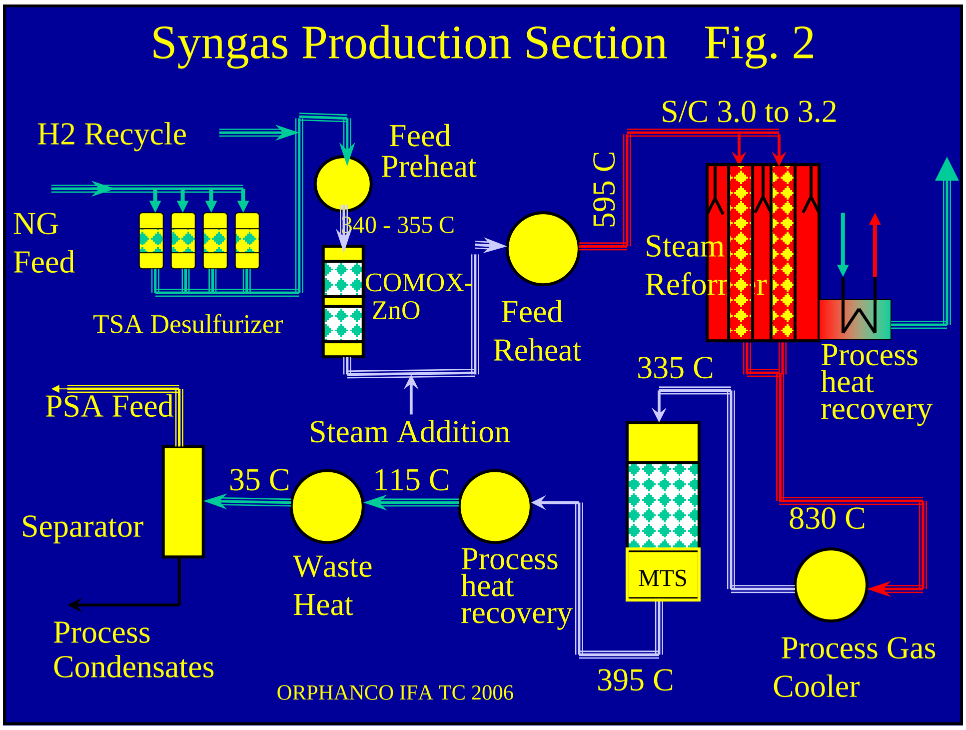
Ammonia Process Block Diagram Fig.1




Syngas Production Section Fig. 2
H2 Recycle
Feed Preheat
S/C 3.0 to 3.2
595 C
NG Feed
340 - 355 C
COMOX-ZnO
TSA Desulfurizer
Feed Reheat
Steam Reformer
Process heat recovery
335 C
PSA Feed
Steam Addition
35 C
115 C
Separator
830 C
MTS
Waste Heat
Process heat recovery
Process Condensates
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395 C
Process Gas Cooler

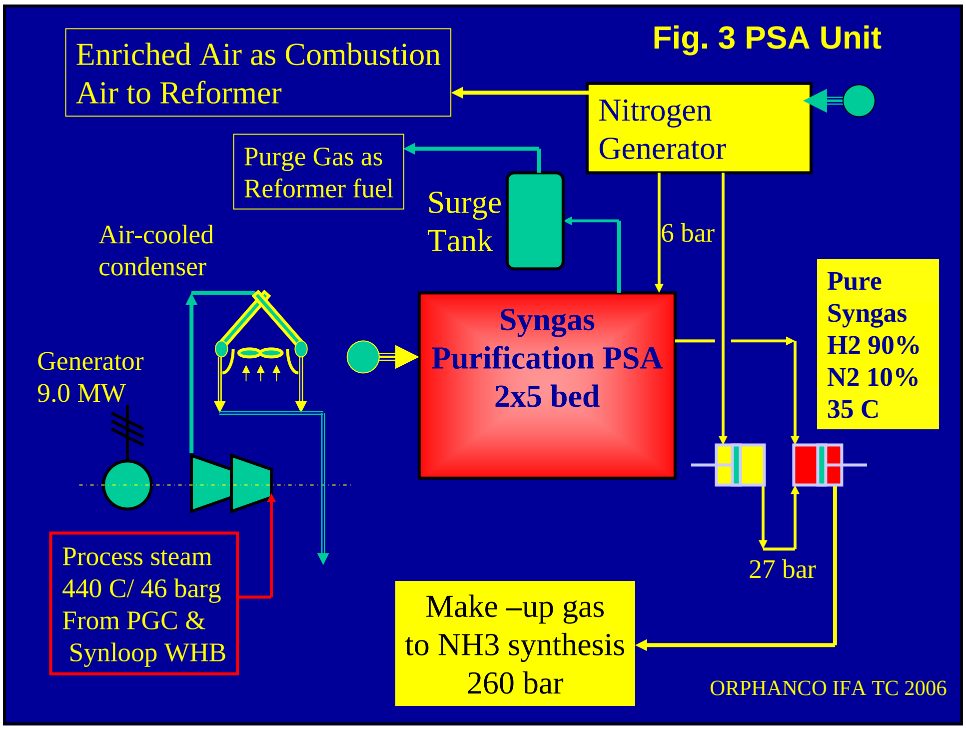
Fig. 3 PSA Unit
Enriched Air as Combustion Air to Reformer
Nitrogen Generator
Purge Gas as Reformer fuel
Surge Tank
Air-cooled condenser
6 bar
Syngas Purification PSA 2x5 bed
Pure Syngas H2 90% N2 10% 35 C
Generator 9.0 MW
27 bar
Process steam 440 C/ 46 barg From PGC & Synloop WHB
Make –up gas to NH3 synthesis 260 bar
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Pressure Swing Adsorption (PSA) Section

- 2 trains 5 bed adsorbent each filled with UOP mol sieves (synthetic zeoliths): two beds in adsorption, 5 in equalizing, 3 in purge / N_2 re-pressurizing
- System's distinct feature is nitrogen purge & first step re-pressurization at 6 bar
- Hydrogen recovery 91.5%. Average $CO + CO_2 + CH_4$ slip < 6 ppm Ar < 120 ppm. ***Pure Syngas !!***
- Properly homogenized low calorific value PSA Purge Gas (1500 kcal/kg), rich in Nitrogen is used as reformer fuel.
- PSA product due to Nitrogen re-pressurization contains 10% N_2
- 1/3 of required for synthesis nitrogen is without energy consumption compressed from 6 to 27 bar.

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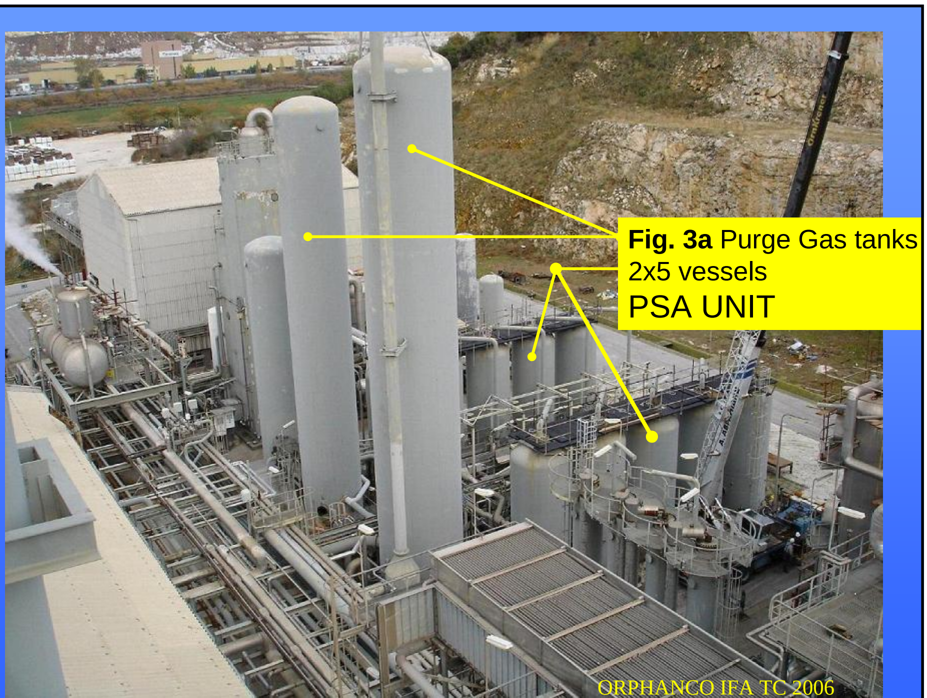

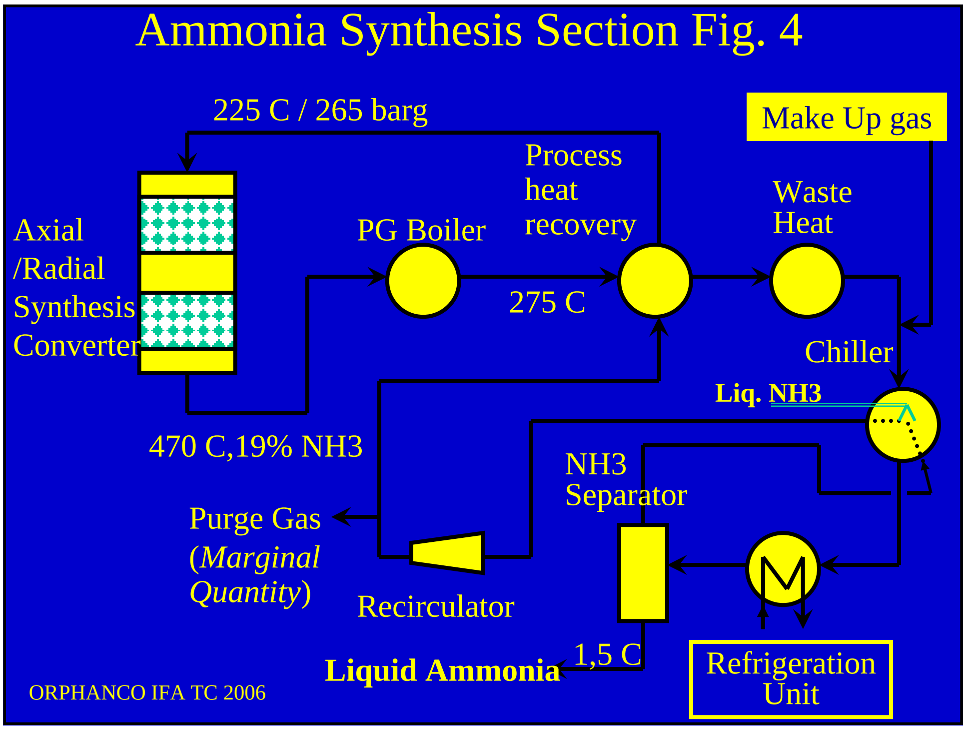

Ammonia Synthesis Section Fig. 4
225 C / 265 barg
Make Up gas
Process
heat
recovery
Waste
Heat
Axial
/Radial
Synthesis
Converter
PG Boiler
275 C
Chiller
Liq. NH3
470 C,19% NH3
NH3
Separator
Purge Gas
(*Marginal*
Quantity)
Recirculator
1,5 C
Liquid Ammonia
Refrigeration
Unit
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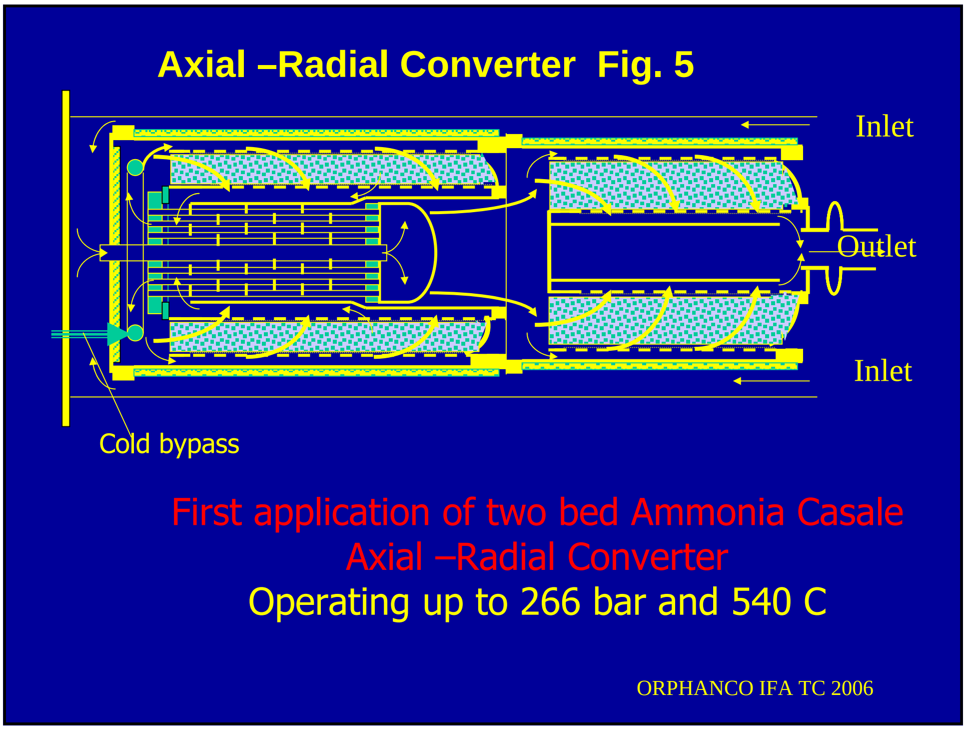

Axial –Radial Converter Fig. 5
Inlet
Outlet
Inlet
Cold bypass
First application of two bed Ammonia Casale
Axial –Radial Converter
Operating up to 266 bar and 540 C
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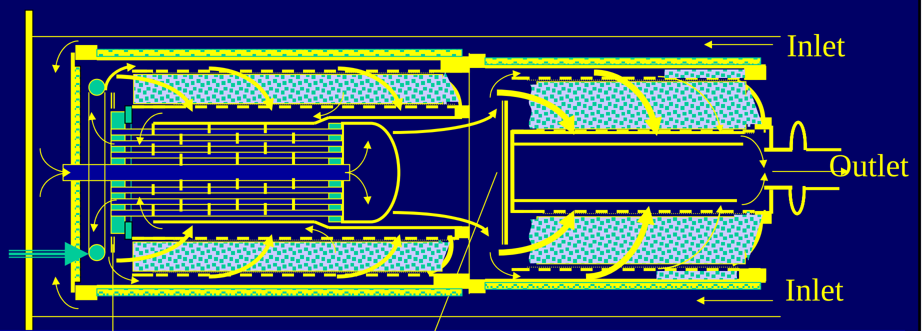
Axial –Radial Converter after 16 years of operation Fig. 6



Lower basket after 16 years operation found with 1/3 of catalyst bed heavily agglomerated and external φ 0.9 mm wire net not well fixed in the top section. Furthermore high gas velocities impinged on top of second bed.

Result : Fine grain catalyst 3-6 mm came out blocking gas path by 1/3 of its length. In spite of that converter was able to make 112% capacity!!!

New impingement plate installed.

New deflector for better mixing installed

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Ammonia Plant main Characteristics

- No Secondary Reformer, No LTS, No Methanator
- Very quick start up
- Purification by PSA mol sieves: High purity Syngas
- No energy consuming CO2/ residual CO/CH4- removal
- Primary Reformer burners designed to use low calorific purge gas from PSA unit and enriched air from Nitrogen Generator
- Process steam to drive power generator covering all motive el. Power requirements
- Air cooled steam turbine condenser
- Practically nil purge gas from synloop.
- Process Steam at MP 45 barg / 440 C

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Many “Firsts” & Innovative Features

- First application of CASALE Axial –Radial Ammonia Converter
- First application of PSA technology for Syngas Purification with innovative N2 recompression (savings in N2 compression energy)
- First application of TSA technology for direct H2S, COS & mercaptans removal by innovative low energy cost regenerative mol-sieves
- Innovative flexible thin tube sheet Process Gas Cooler with ***external*** low temperature by pass
- Innovative thin tube sheet, low alloy Synloop WHB. Inlet gas 470 C /265 barg. High specific steam production: 1.35 MT/ 1MT NH3
- Natural gas is used only as Pr. Reformer feed

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History since spring 2001

- Ammonia Prices have shown extreme volatility of +/- 40% in less than a month
- Product over-capacity, seasonal demand, global economy down turn being the main reasons
- Natural Gas Prices followed a more stable pattern
- With 85-90% of variable production cost being the cost of NG => Ammonia Unit Profit Margins swinging from positive to negative and backwards !

Unit Operating on a Start Up / Shut Down Cycle

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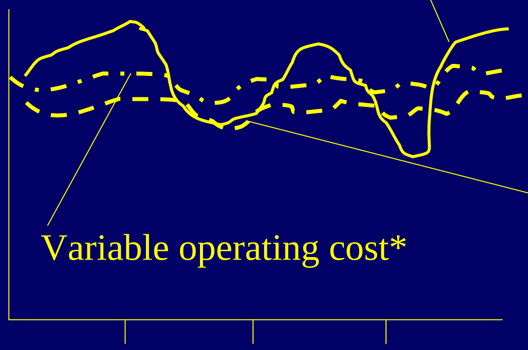
Ammonia price volatility Fig. 7

Ammonia price FOB Yusny

- seasonal demand
- energy prices
- over-capacity
- large traded volume by small storage capacity



Reduced operating cost >>avoid one shut down

Variable operating cost*

* 90% of variable cost = N.G cost

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Action Plan Set Forward

- New Operating Strategy, focusing on minimizing operating costs and maximize energy efficiency rather than maximizing production
- Develop coherent conservation (mothballing) program for the process equipment when plant in standstill
- Develop an optimal Start Up / Shut Down pattern.
- Adapt plant staffing requirements to seasonal plant operation (low ammonia price during summer >> annual leaves)
- Investigate the plant's mid to long term future

All the above with very strict budget limitations !

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Energy Efficiency Maximization (1)

Hydrogen Production Section, based on unit's simulation and pinch analysis results:

1. S/C Ratio in Primary Reformer Feed, initially decreased from 3.45 to 3.1 mol/mol
2. Tighter firing control in Primary Reformer (average excess air at 5% from 15%).
3. Increase of BFW inlet temp in deareator from 90 to 95 C.
4. Increase in Desulphurizer inlet temp from 340 to 355 C.
5. Increase of PSA subcycle time from 76 to 80 sec.

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Energy Efficiency Maximization (2)

Ammonia Synthesis Section

1. Purge Minimization
2. Product Separator Temperature Decrease
3. Heat Recovery Maximization (Pinch Analysis)
4. Replace Synthesis Catalyst

Power Generation Section

1. Evaporative Cooling in Steam Turbine Air Condenser

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Energy Efficiency Maximization (3)

- Specific Energy Consumption Improvement: 7.2 Gcal/MT from 7.40 Gcal /MT
- Some further energy efficiency improvement considerations:
  - Advanced control technology for Reformer Firing
  - Automatic Control of Synthesis Section Purge
  - Advanced Control technology for N2/H2 mixture control
  - NG and Syngas Flaring minimization during start up / shut down

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Equipment Mothballing Program

Task: According to shut down projections develop a coherent Mothballing program for the equipment based on the following guidelines:

- Mothballing program should provide “maximum” safety to equipment
- Plant recommissioning possible in less than 15 calendar days
- When plant is shut down during the winter mothballing program must provide winterization protection
- Develop maintenance program to be performed during plant standstill

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Focus Areas (1)

- Catalytic Reactors and Mol Sieve Vessels:
  - Kept under N2 blanket
  - Close monitoring, at least two pressure readings and temperature readings
  - Appropriate blanketing and fixed N2 addition construction
- Steam System: This includes, boilers, H.P. steam piping and steam superheaters.
  - Kept under closely monitored N2 blanket.
  - Dry preservation preferred over wet because of ability to purge system while hot, low cost of N2, and winterization considerations

Focus Areas (2)

- BFW+Dearaetor+LP Steam: Critical Parts of the system in N2 blanket (mainly the deareator). The rest was thoroughly purged+dried and was kept under dry air blanket
- Cooling Water System: Challenging part due to complexity of system, mixed metallurgy and corrosion potential and varying criticality of different parts of the System
  - System drained and purged with dry air
  - Accessible points opened for inspection and cleaning
  - Criticality assessment of equipment:Critical equipment blinded and kept under N2 blanket
  - All other water coolers purged with N2 and simply isolated

Focus Areas (3)

- Rotating Equipment:
  - All rotating equipment was following a periodic rotation program.
  - Problems were recorded in special log sheets.
  - Special Considerations were given to large rotating equipment (extra blinding, purging, parts removal)
- Control Valves:
  - Control valves were following a periodic open/close program.
  - Problems recorded in special log sheets
- Thermal Insulation: Critical Issue, but all to often overlooked.
  - Detailed inspection of insulation, repair-sealing where possible, removed in cases

Plant Recommissioning

- Thorough inspection and leak test of process piping
- Special NDT inspection schedule for process equipment and piping. Focus on problems occurred by long standstill, such as corrosion under insulation
- Piping and equipment flushing when CW and steam systems are put back into operation
- Check and tuning of safety system hardware (switches)
- Check of operational status of instruments, alarm settings at DCS, PID controllers tuning, and ESD system
- Functional tests on various systems
- Running tests on rotating equipment

Plant Back Online

Concluding Remarks

- By reducing operating cost some shut down can be avoided
- Plant had four (4) cold Start Ups since May 2001, with only minor occurrences and all meeting production schedule
- Operating history shows that operating an Ammonia Unit on a Start Up / Shut Down Cycle is technically feasible
- Short to Mid term studies show that under current market conditions such operating cycle makes economical sense
- Such operating pattern led to the quick adaptation of much needed modern operating practices, which would otherwise meet vigorous resistance

Main performance highlights after 16 years operation at 115% design rate short before turnaround on November 2005

- Casale Ammonia Synthesis converter with the same catalyst at optimum performance in spite of 1/3 of 2nd converter basket catalyst bypassed!
- PSA mol-sieves with the same performance efficiency, delivering very high purity Syngas at 91.5% Hydrogen efficiency
- Reformer tubes in operation since 1985 [120000 h] without tube failure
- Process Gas Cooler and Synloop WH Boiler in operation without tube, or other kind of failure on pressure bearing parts
- Minimum cost for catalysts inventory
- Minimum operating cost for Syngas purification
- Nitrogen generator with almost 100% reliability in 18 years operating time

Cont'd

Main equipment condition after 17 years operation at 115% design rate

- Reformer tubes after 120,000 hours operation with minor findings only, according eddy current and laser NDT. Remaining life estimated to about 40,000 h. Only two tubes preventive replacement for microscopic examination.
- Process Gas Cooler tubes Eddy current & IRIS examination shown only one tube with remaining life of 4 to 5 years. Remaining life of all other tubes estimated to be longer than 8 years.
- Process Gas Cooler innovative external bypass in good condition: only moderate metal dusting in the mixing sleeve (inconel 601 replaced by 602)
- HIMA based ESD provoked one partial plant shut down only in 17 years

Con'd

Main equipment condition after 17 years operation at 115% design rate *Cont'd*

- Synthesis thin tube-sheet WHB tubes Eddy current & IRIS examination shown no damage, or excessive wear. Remaining life estimated to more than 10 years
- PSA adsorber vessels after about 500,000 pressure cycles from 1 to 28 barg not showing signs of fatigue. Mol sieves after 16 years operation - 4 years mothballing showing no aging!
- PSA Kuhme on-off valves with more than 30000 h MRTBF
- PSA PLC (Modicon) shown no failure in last 8 years of operation
- Piston rod – Teflon guiding rings of high pressure syngas compressors records breaking running times 100,000 hours!!. Piston Rings running time 50,000 hours at 250 bar operating pressure