



# Improved Hard Process

*Best Available Technology for Producing High Grade Phosphoric Acid from Lower Zone Phosphate Ore in the Florida Southern Extension*

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# Summary of Improved Hard Process (IHP) Advantages Over the Wet Acid Process (WAP), Particularly for Producing Phosphoric Acid from High MgO Phosphate Raw Materials from the Lower Zone of the Florida Southern Extension

1. Smaller Environmental Footprint
  - NO Gyp Pile
  - Reduced Tailings Pond
  - Less Water Usage
2. Resource Stewardship
  - Increased Mine Yield (up to 2 times for Southern Extension)
  - Plant Nutrient Delivery Efficiency Through Fertigation Products
3. Cost Advantage
  - SPA
  - MAP/DAP synergies
  - Water-Soluble Dry Products (super MAP and DAP without sludge).
  - Merchant / Tech / Food Grade

Note: At \$100 Sulfur IHP retains a 2X cost advantage over WAP for making SPA

# The Wet Acid Process (WAP) and Furnace Acid Process (FAP) each have Advantages/Disadvantages in Making Phosphoric Acid

- WAP

- Advantages: Cheapest commercialized technology.

- Disadvantages: Requires high grade beneficiated ore; makes impure, dilute black acid; uses copious amounts of water; has environmental problems which include large gypsum piles and clay ponds.

- FAP

- Advantages: Can use ores without beneficiation; makes high-purity, water-white acid; requires limited water usage; produces solid waste that does not leach impurities and holds radioactivity in stable form.

- Disadvantages: Costly due to large electrical usage and the requirement that the raw material feed to the process be clinkered.

*Can we commercialize a phosphoric acid process with the advantages of the FAP, but without using large amounts of expensive electricity?*

- **Yes**, such a process already exists; the Blast Furnace Process operated commercially in the US for twelve years beginning in the 1920's.
  - Process had very poor heat integration (5x theoretical coke is required), and had such large recirculating gas flows that the process was not economically superior to the FAP.
- But the process worked, proving the thermal process concept without *in situ* resistance heating of the process solids with electricity.

# We Must Modify the Question

*Can we commercialize a “thermally efficient” phosphoric acid process with the advantages of the FAP, but without using large amounts of electricity?*

- **The “Improved Hard Process” answers this challenge**

- High thermal efficiency.

- Uses lower quality ores, sometimes directly as-mined matrix, without beneficiation or washing.

- Produces a pure, concentrated, phosphoric acid product.

- Attractive environmental footprint.

- Cheaper for most ores than the WAP.

- **Can process with higher overall yields relatively high magnesium ores, not currently mined, from the lower zone of the Florida Southern Extension, thereby doubling mine productivity.**

# History: Other Thermal Processes Not Using Electrical Resistance Heating

- Blast Furnaces- 1920's , Commercial, Not quite Economic over FAP.
- FMC- 1960's , Kiln Process, Failed, Melting; Dead.
- Olin- 1970's, Kiln Process, Operating Difficulties; Dead.
- Megy- 1978, Kiln Process, Failed, Melting; Dead.
- Hard- 1982 Pilot Proven, Near Economic verses WAP.
- Russian: - Not Kiln Process- Charge Melts-Economics suspect and depends on byproduct value-not proven.
- Chinese:- CDK-Kiln Method 2005, 10x size Hard Process Semi-Works Plant with “coated balls” and “electrostatic phosphoric acid collector”, not continuously operable, requires slag be used in making cement for economics to work.
- **Improved Hard Process (IHP):**
  - **Highest thermal efficiency**
  - **Pilot Proven / Patented**
  - **Best economics- doesn't depend on byproduct credits.**

# Comparative “Base Cost” With Other Processes

<u>Item</u>	<u>IHP</u>	<u>Chinese</u>	<u>Russian</u>	<u>WAP</u>
Sulfur, \$73/st				75
Phosphate, \$37/st			<b>130</b>	134
Matrix, \$17/st	67	67		
Silica, \$7/st	17	39		
Bauxite, \$27/st			111	
Anhydrate, \$25/st			10	
Oxygen, \$70/MCM			98	
Green Coke, \$30/st	21	<b>33</b>	<b>61</b>	
Electricity, \$0.08/kwh	31	46	13	11
Nat Gas, \$13/MM BTU	16	104	53	
Other Process	77	<b>77</b>	77	77
Convert to SPA				<u>110</u>
<b>Total</b>	<b>\$ 229</b>	<b>\$ 366</b>	<b>\$ 553</b>	<b>\$ 407</b>
<u>Credits</u>	<u>A</u>	<u>C</u>	<u>SG,C</u>	<u>G</u>

C=Cement A=Aggregate SG= Syngas G= Gypsum

# Pilot Plant Results – Hard Process 1981-2

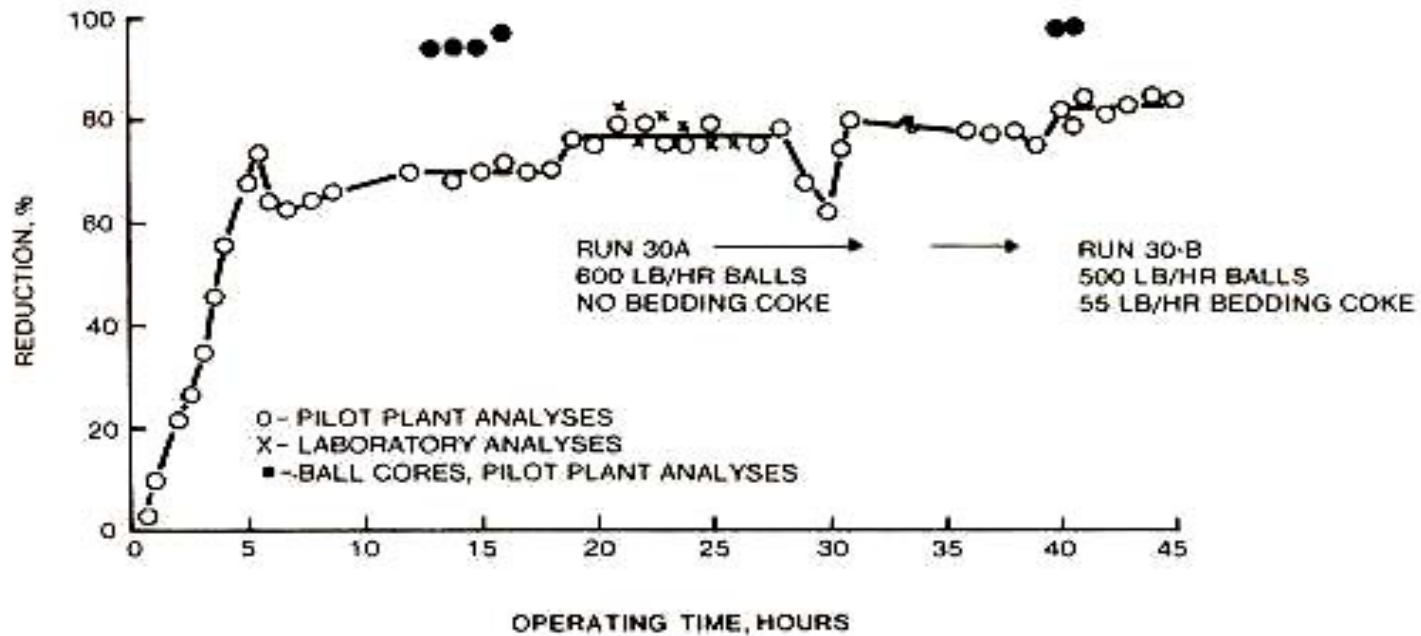
## Successes:

- Up to 1,000 pounds per hour processed.  
Limited by kiln design, not the process.
- Had consistent yields of 75-87%.
- Made acid in hydrator.
- Operation up to 1500 °C; without melting problems.

## Problems:

- Hot spot in kiln limited performance.
- Used calcined coke rather than green coke.
- Used coke at two times theoretical to reduce phosphate.
- High silica (low  $P_2O_5$ ) in kiln feed.
- Reducing off gas; afterburner required.
- Engineering estimates showed the Hard Process was not quite competitive with Wet Acid Process.

# Pilot Plant gave reliable, reasonable yield in long runs over a one month period of operation



**Figure 12.** Continuous pilot plant runs; reduction history, runs 30A and 30B.

# Research Portion of Kiln Program

1977-82 2001-08

Project Manager	Megy	Megy
Professionals	15	2**
Total Budget (\$10 <sup>6</sup> )	5	0.2
Location	Irvine, CA	Richland, WA
Institution	ORC ****	PNNL***
Process	Hard	IHP*

\* Improved Hard Process.

\*\* Plus outside advisors and technical team.

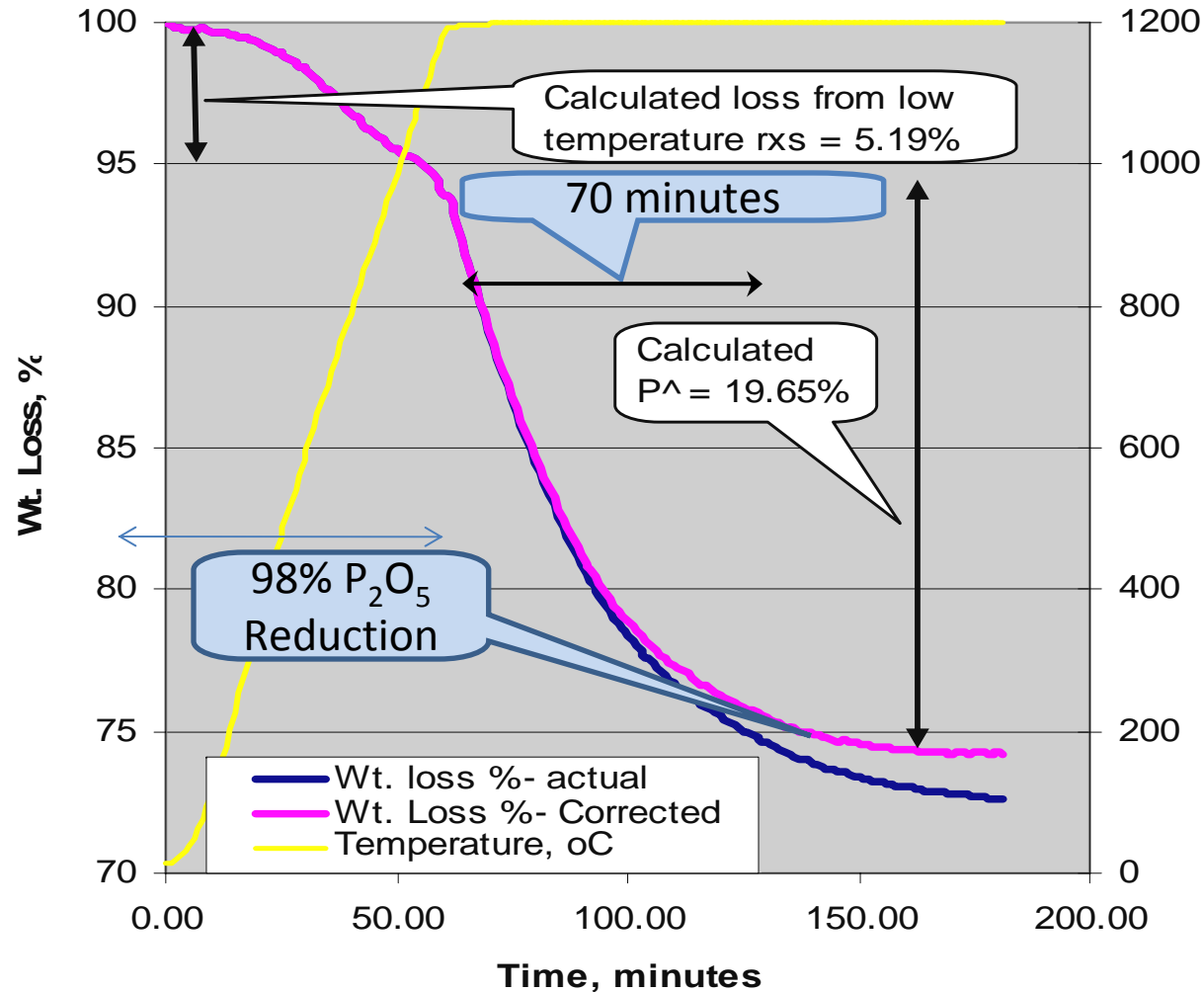
\*\*\* Pacific Northwest National Labs.

\*\*\*\* Occidental Research Laboratories.

# Recent research program give four major discoveries and several minor ones that greatly improved the Hard Process

- Improved Hard Process compared to Hard Process:
  - Improves phosphoric acid production rates by a factor of five in a given sized commercial kiln.
  - Substantially increases phosphate concentration in the kiln feed reducing grinding and other processing cost.
  - Improved phosphoric acid yield from 70-85% range to mid 90% range.
  - More efficiently uses coke, and can use cheaper, high sulfur green coke.
  - Gives oxidizing kiln off-gas with elimination of afterburner requirement.

Research shows specification to economically make feed agglomerates that will give high phosphate yield at 1200 °C.



# Research Identifies Ore Requirements

- Iron (and other transition metals) Impurities
  - ✓ Reduces yield by forming ferrophos which stays in the kiln solids.  
1.5%  $\text{Fe}_2\text{O}_3$  reduces yield about 2%.
- Magnesium and Calcium Carbonate Impurities.
  - ✓ Requires more silica to offset.
  - ✓ Up to 2% MgO tolerable.
- Alumina Impurities
  - ✓ Promotes melting
  - ✓ Up to 2%  $\text{Al}_2\text{O}_3$  tolerable.
- Water in Matrix ore feed material
  - ✓ If >10%, extra fuel is required and rapidly becomes cost prohibitive.
  - ✓ Wet ore requires washing to remove clay and associated water.
- Clay (approximately 5%) is required as a binder.
  - ✓ 0.7% bentonite can be used instead, but costly.
- Silica, clay, and organics in the matrix benefit the process.

# Vendor Testing (Basis for Quotes)

1978-82 2002-08

Batch Ball mill Tests	3	2
Continuous Ball Mill (days)	50	3
Mixer/Balling Pan Tests	3	2
Cont. Mixer/Ball Pan (days)	50	2
Grate drying tests	3	2
<b>Batch Kiln Tests</b>	70	<b>19*</b>
Continuous Kiln Tests (no)	7	0
<u>Budget (\$ 10<sup>6</sup>)</u>	7	0.2

\*Research focused on “Carbon Burnout” and “Kiln Temperature Profile Control”

## Vendor Pilot Tests give specifications to economically make agglomerates like this



# Florida IHP Mass Balance Southern Extension Case

<u>Stream</u>	<u>P<sub>2</sub>O<sub>5</sub></u>	<u>CaO</u>	<u>MgO</u>	<u>SiO<sub>2</sub></u>	<u>Fix C</u>	<u>t/t P<sub>2</sub>O<sub>5</sub></u>
Pebble LZ	20	36	4	15.1		1.57
Conc LZ	27.8	42.4	1.64	5.2		1.42
Feed LZ	6.7	11.4	0.79	72.8		5.21
Clay UZ	6.1	13.2	1.7	51.4		0.44
Green coke					83.0%	0.72
Ball	11.6%	19.4%	1.4%	46.3%	6.4%	9.35

# Production Cost of WAP and IHP

- Add 200,000 st P<sub>2</sub>O<sub>5</sub>/yr to existing commercial site

Plant Idaho, \$/st Florida, \$/st

IHP (72% white acid)***	<b>\$260</b>	\$280
WAP (26% black acid)	\$799*	\$666**
<u>WAP (72% SPA)</u>	<u>\$909*</u>	na****

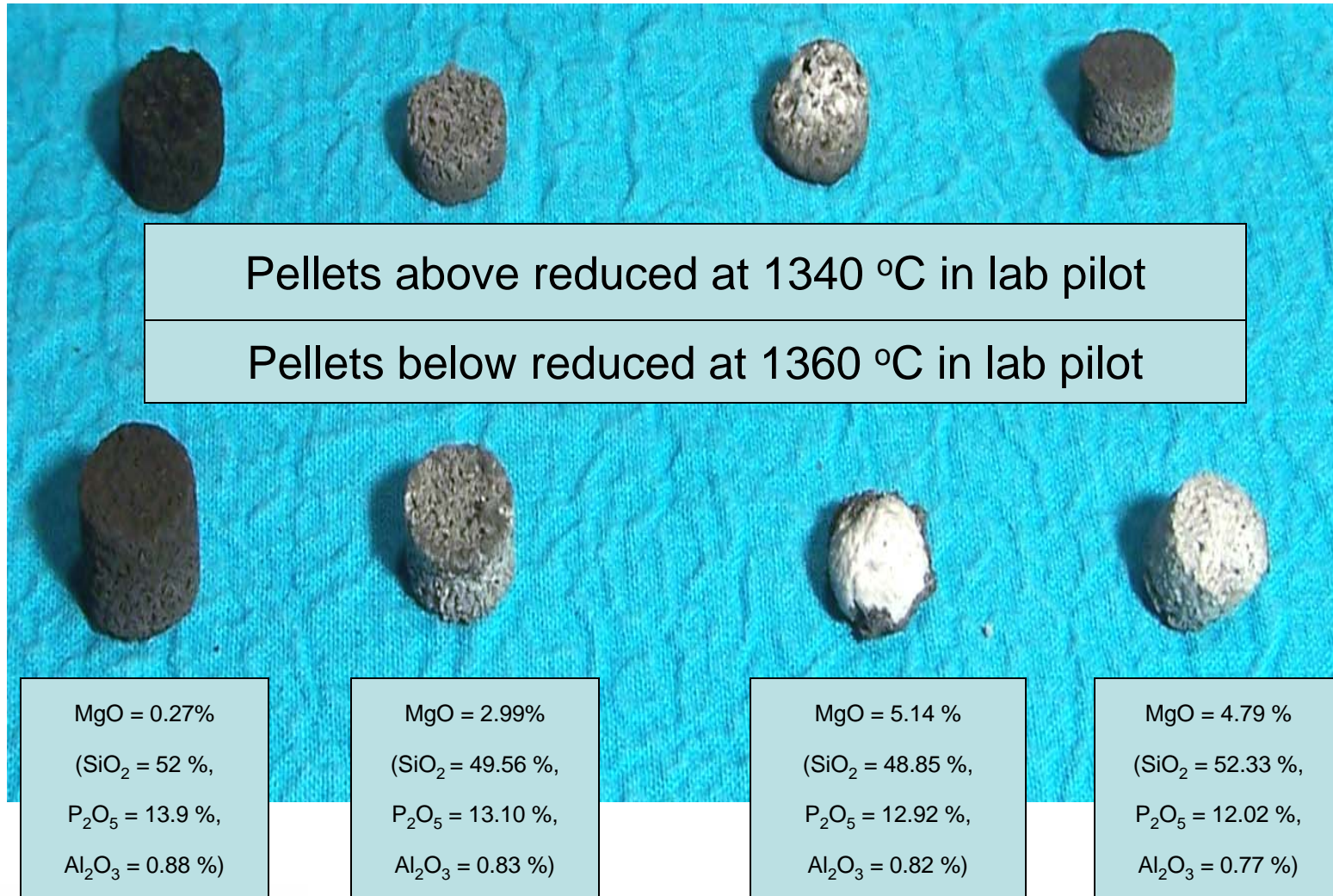
\* Sulfur at \$600/st

\*\* Sulfur at \$450/st

\*\*\* Green Petroleum Coke at \$100/st

\*\*\*\* High magnesium ore precludes economic manufacture of SPA in Southern Florida.

# Can the 2% MgO of the Lower Zone Avoid Melting Problems in the Kiln?

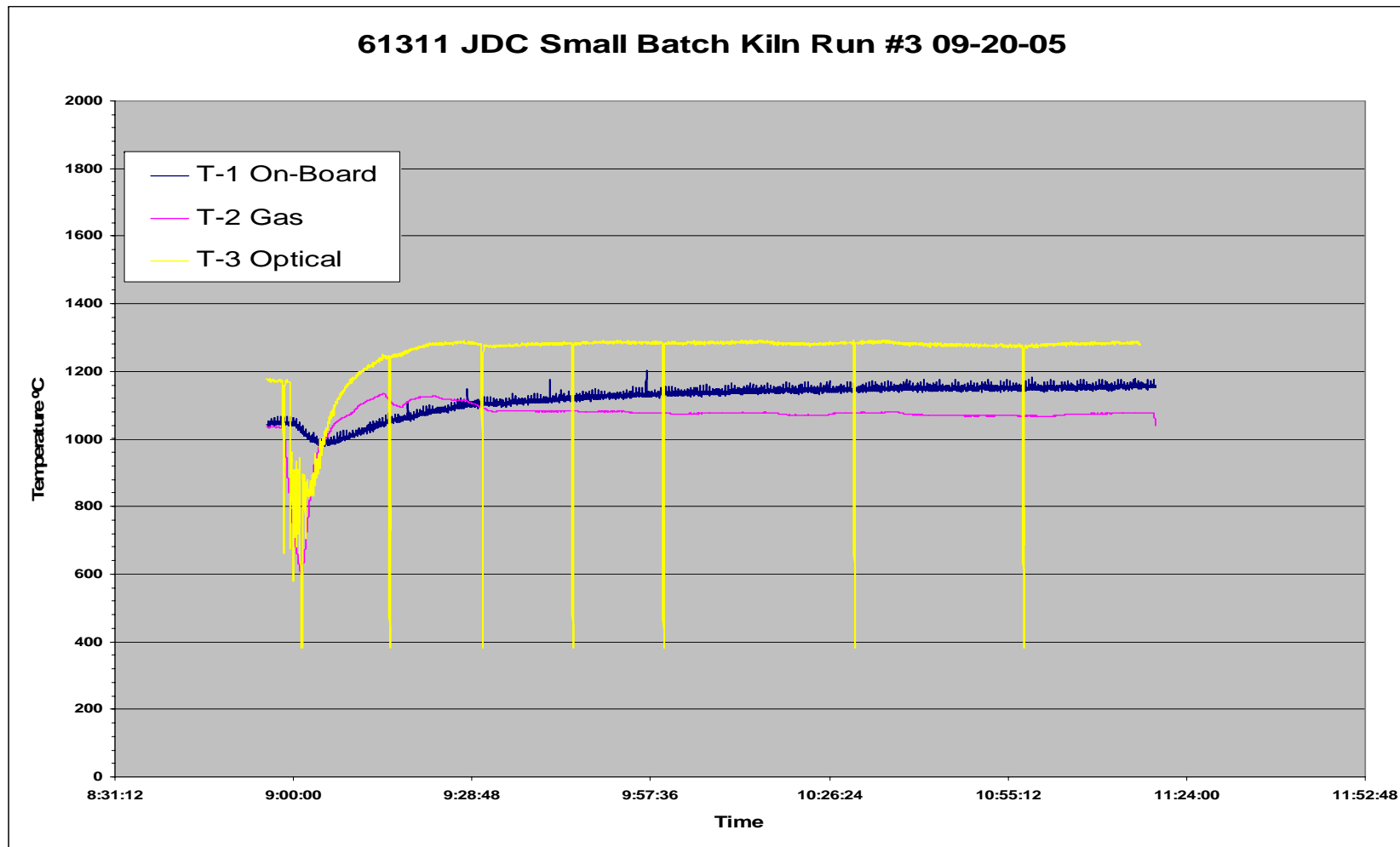


# Has the Temperature Stability Problem been Overcome?



Batch Kiln Testing at Vendor Laboratory

# Yes, JDCPhosphate has Developed and Proved Methods of Holding Kiln Temperature +/- 5° C in Batch Kiln Tests



# What is the next step in commercialization of the IHP?

- Pilot Plant of process is complete with ORC pilot.
  - Process lined out 31 times over one month of operation.
  - All improvements within temperature and compositional limits of pilot plant testing.
- JDCPhosphate comfortable with factor of ten scale up of the process to a Semi-Commercial facility.

# Issues to Resolve in Semi-Commercial Facility

- Maximize ultimate throughput for each system component.
- Maximize ultimate kiln yield.
- Minimize coke requirement.
- Gain Operating experience.
- Gain Maintenance experience.
- Resolve detailed environmental requirements.
- Characterize and optimize product impurity levels.
- Refine equipment specifications.
- Develop Detail work instructions.
- Develop optimal downstream customer relationships.

# Do we have confidence in our capital and operating cost studies?

- 1978-82
  1. ORC In-house Factored
  2. Kaiser Mexican Level 3
- 2004-08 US Dept of Ag SBIR Grants
  1. Semi-Commercial Level 3
  2. Commercial Factored

# New Opportunities: *Resource Sustainability* Southern Florida Phosphate Industry

- Improved Mine Yield (2X)
  - Use Lower Zone ore currently not mined.
  - Significant use of float feed without beneficiation yield losses.
  - Some use of clay.
- Fertigation product target.
  - Product directly used in preparation of liquid fertilizers for use in fertigation.
  - Product may be crystallized to “super MAP” and “super DAP” for use in fertigation.

# New Opportunities: *Environmental* Southern Florida Phosphate Industry

- No Gyp Piles. (Co-product is a glassy inert aggregate)
- Reduced Tailings Ponds (partial beneficiation).
  - Uses Some Clay with residual  $P_2O_5$ .
- Reduced Water (dry process).
- No Sulfuric Acid Plant Needed.
- Reduced Mine Footprint (2X Yield)

# New Opportunities: Cost

## Southern Florida Phosphate Industry

- IHP produces high quality, concentrated phosphoric acid (72%  $P_2O_5$ )
  - Liquid Fertilizers suitable for fertigation
  - “Super MAP” and “Super DAP” crystallized solid fertilizer which dissolve without residue formation and suitable for fertigation.
  - May allow for simplified preparation of food grade acid without the without the need of an expensive solvent extraction requirement.
  - IHP product acid may be able to be combined with black acid from the WAP to give a more concentrated phosphoric acid suitable making granulated MAP and DAP without and evaporation requirement.
  - The cost of IHP phosphoric acid is projected to be cheaper than WAP black acid.
  -

# Future of the IHP

- Research and Development of the IHP process was substantially complete in 2005.
- JDCPhosphate is an R&D company that wishes to work with the existing phosphate industry to commercialize this process.
- JDCPhosphate is discussing this process with prospective partners worldwide.
- The most advantageous place to use the IHP is in the Florida Southern Extension to process the high MgO ores of the lower zone.
- The IHP advantages of extended resource sustainability, improved product quality, lower cost, and reduced environmental footprint require the attention and support of the phosphate industry.

# Acknowledgements

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