“Innovations and Actions to Improve Efficiencies and Prevent Pollution in Fertilizer Production.”

Beijing, China, June 20th 2013

Vaughn Astley

Dr Phosphate, Inc.

Ex A&W, Freeport McMoRan, Agrico, & IMC

What Has the Industry Done to Improve P Efficiency??

January 17th 1903

Around Tea Time

- **Well!!! Initially they just screened the Pebble from Rivers and threw the undersize away!!!!**

Progress

- **Only Pebble was retained, discarded all material below 1mm/ 16 mesh i.e. Discarded feed +300 microns and, clays < 300 microns.**
- **By 1927 development of flotation, which separates phosphate rock from sand.**
- **Since 1942, most mining advancements have been in refining the dragline mining and flotation processes.**
- **Much of today's reserves are left in the ground because the dolomite, which contains magnesium, causes problems at the fertilizer processing plants.**

Typical Florida Mine Reserves

- **11,000 available acres for mining**
- **9,000 mineable acres (80%) Why!!**
- **5,500 product tons/acre (Splits!!)**
  - **39% pebble**
  - **61% concentrate**
- **3.42 matrix-x (cubic yards of matrix/ton of product)**
- **13.72 total-x (total cubic yards moved/ton of product)**

Reserves

- 18.1 BPL feed grade
- Beneficiated to:
  - 67.8 BPL eg. 67.8 / 18.1=3.74x
  - 0.49 MgO
  - 2.10 I&A
  - 0.084 MER
- 48 MM tons of product (9000ac x 5500t/ac)
- Waste products are
  - 52 MM tons of clay
  - 107 MM tons of tailings

P Efficiency?

- **Don’t lose it in the first place**
  - **Geology**
  - **Smart Mining**
  - **Other Smarts**

Geology

Core Assessment Defines what is Mined Based on BPL and MgO

MgO is Bad for Phosacid and DAP/MAP Manufacture

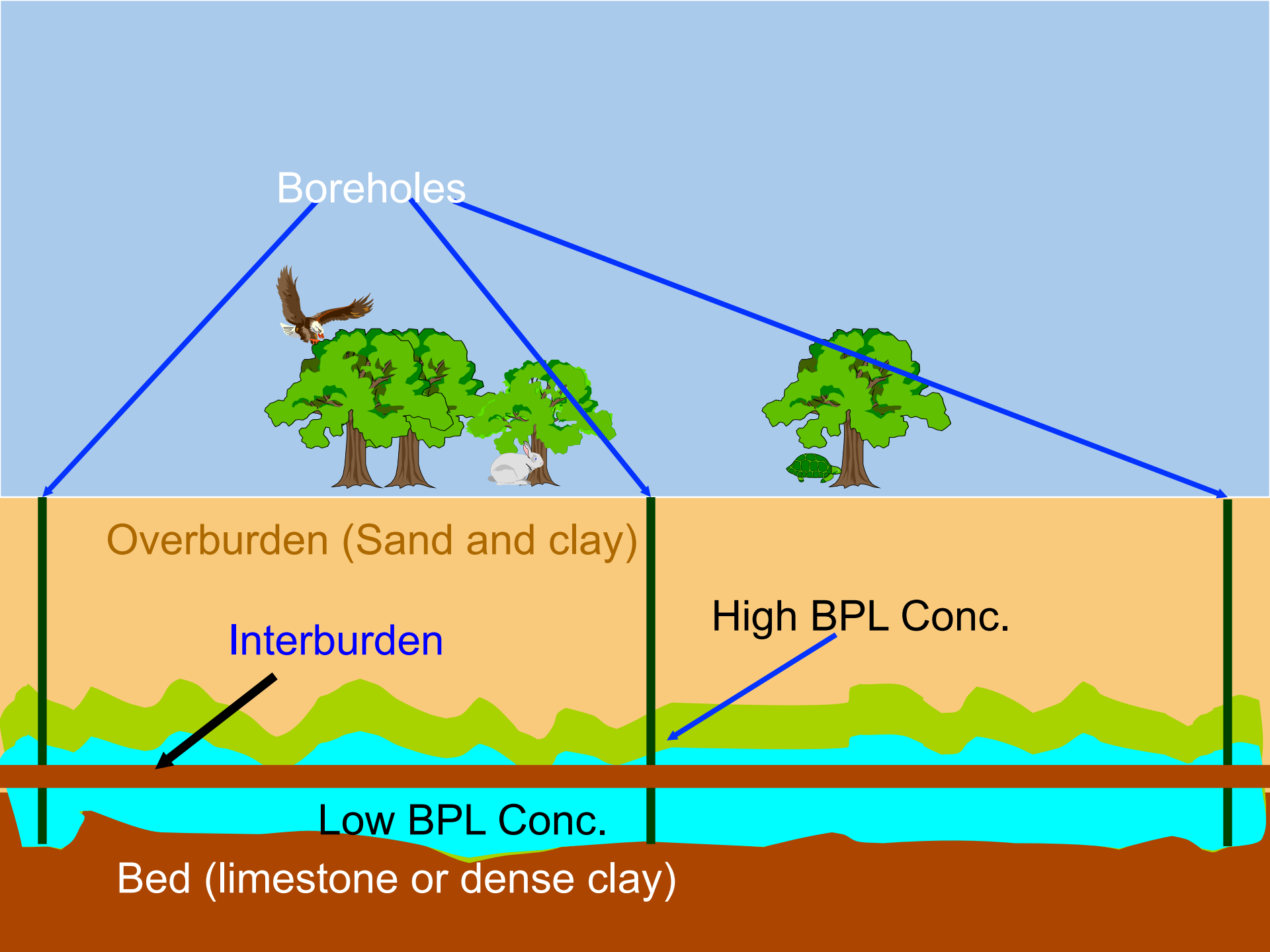
Redefining What We Know

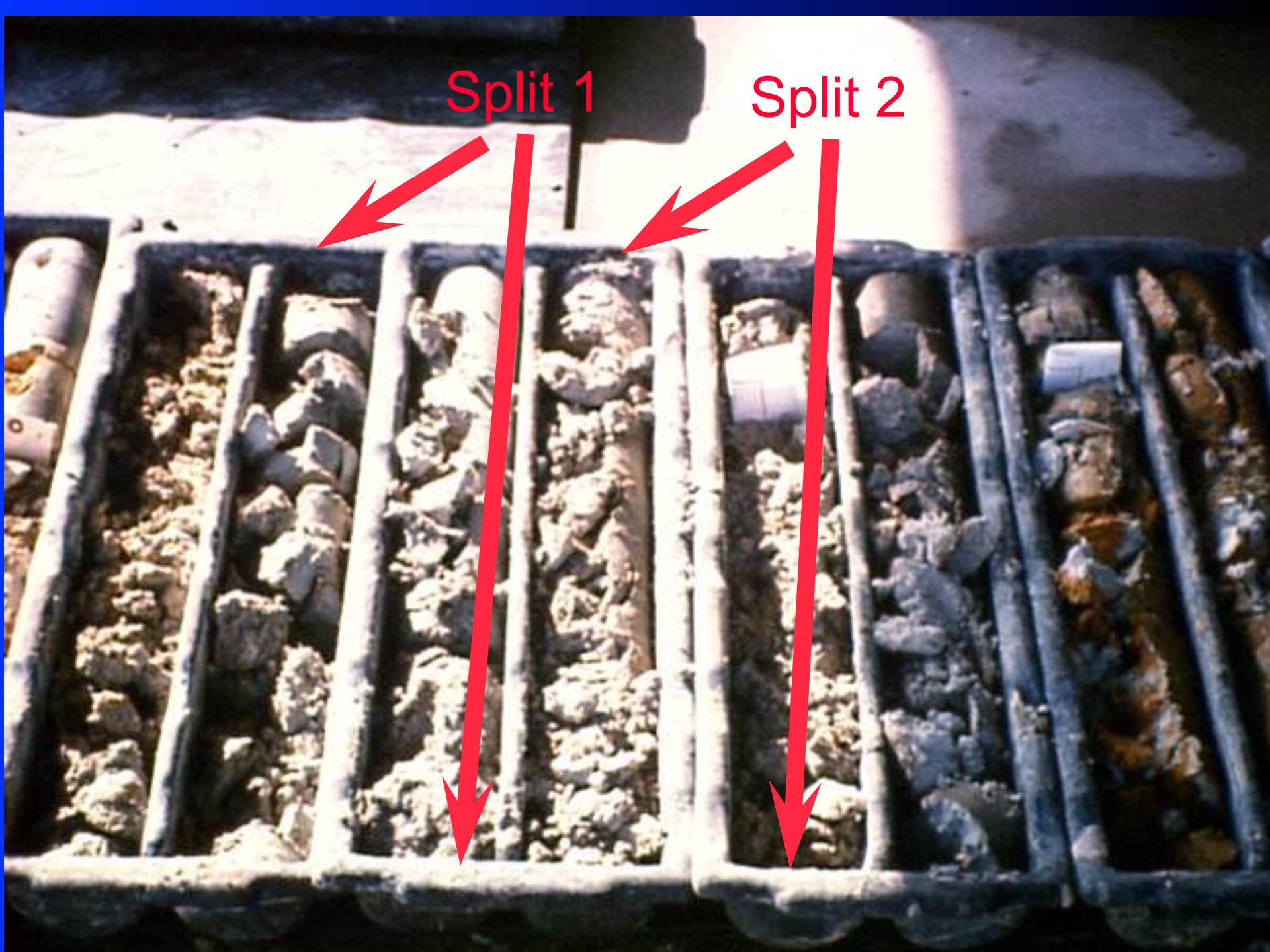
Distribution of MgO in Florida Phosphate Deposits

Based on Drill Core Data

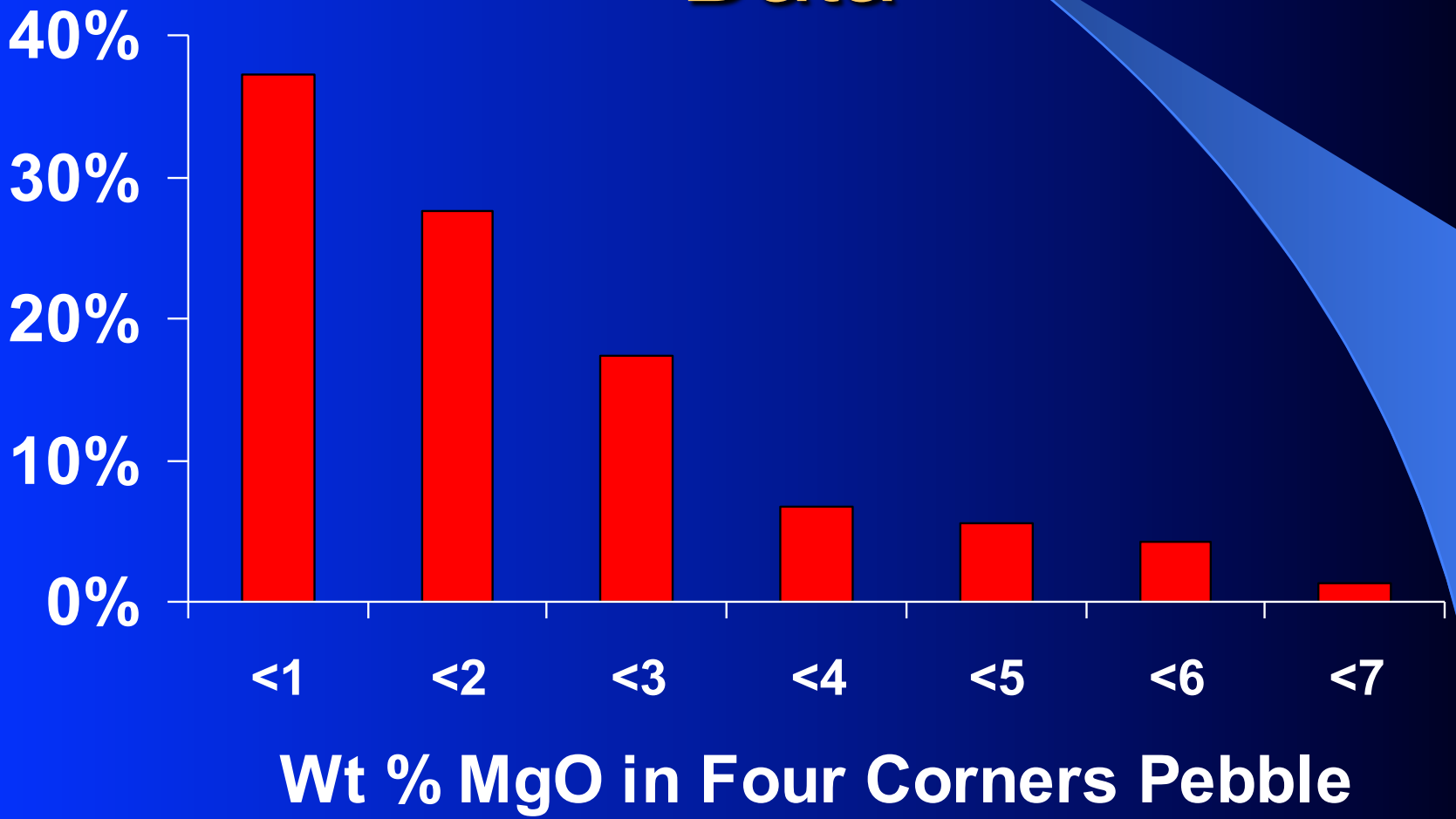
Rock Resource Information

- **Data is Obtained From Drill Cores**
- **Typically 300 ft spacing's**
- **Drill Cores Are Typically 4 Inches in Diameter**
- **Cores Are Analyzed by “Splits” to Obtain Adequate Samples for Beneficiation Tests**
- **Splits Are Determined by Geologists Based on Visual Differences**

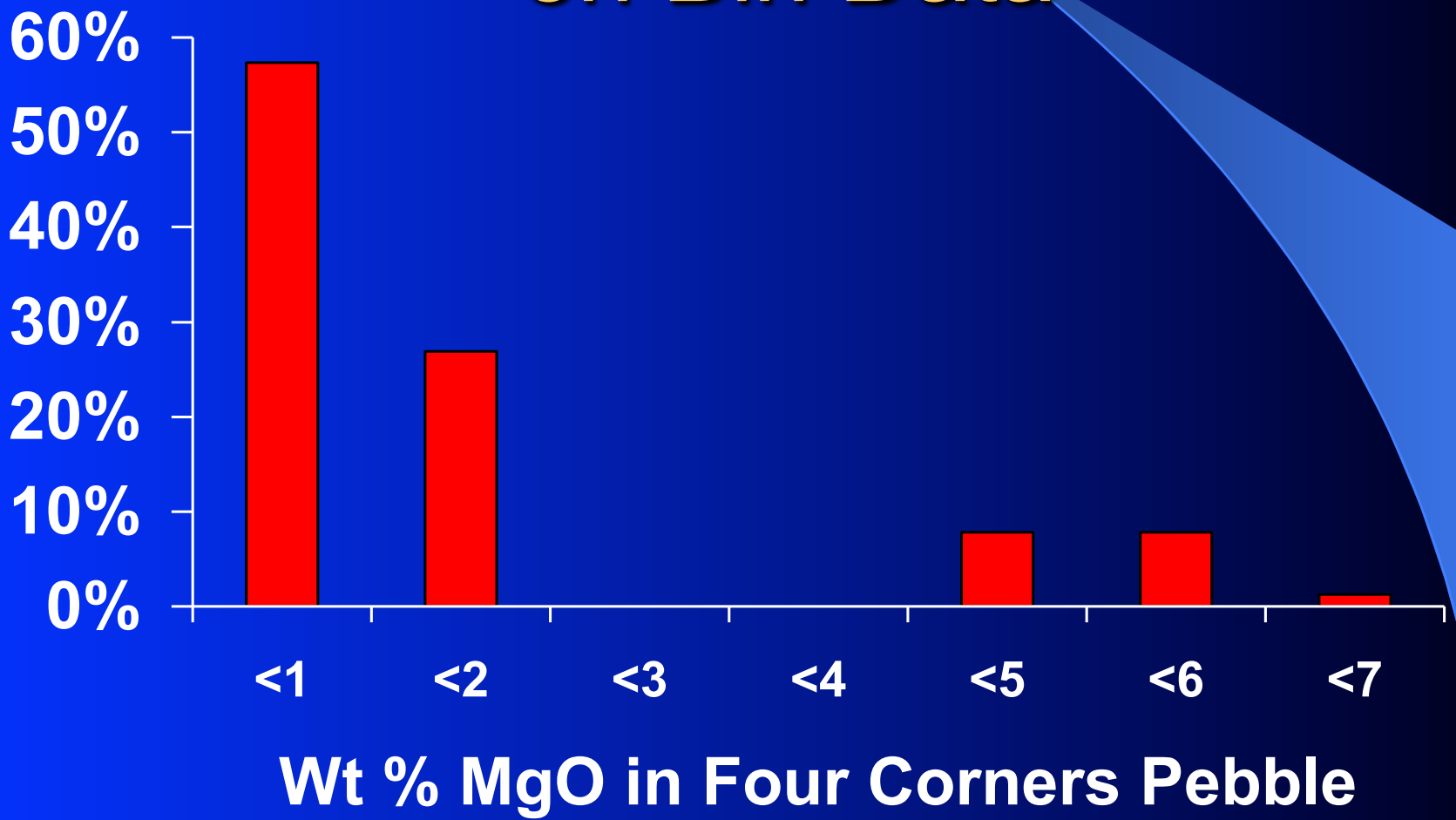

Boreholes
Overburden (Sand and clay)
Interburden
High BPL Conc.
Low BPL Conc.
Bed (limestone or dense clay)


Split 1
Split 2

Distribution of MgO in Pebble Based on Drill Core Data



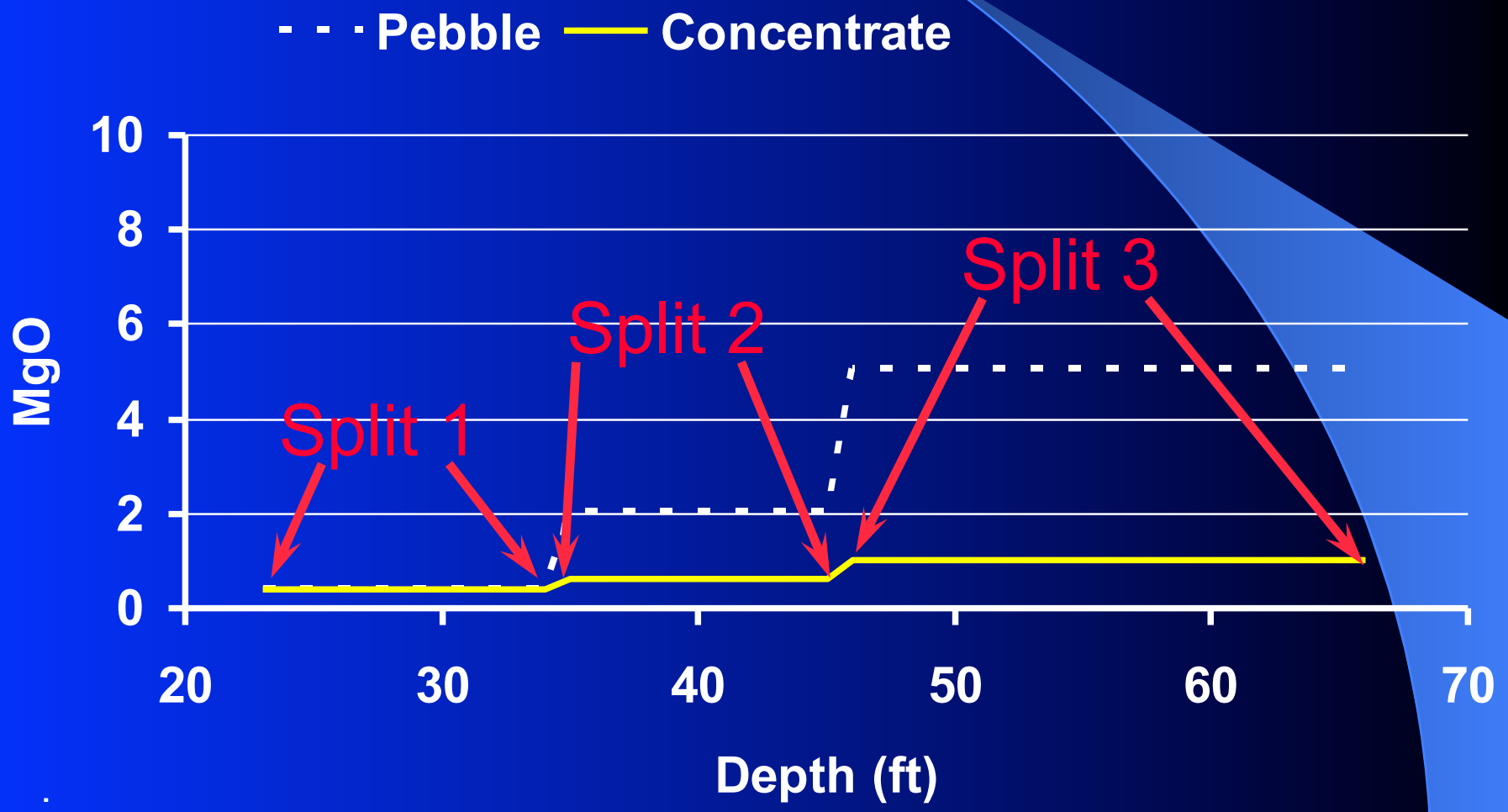
Distribution of MgO Four Corners Pebble MgO Based on Bin Data



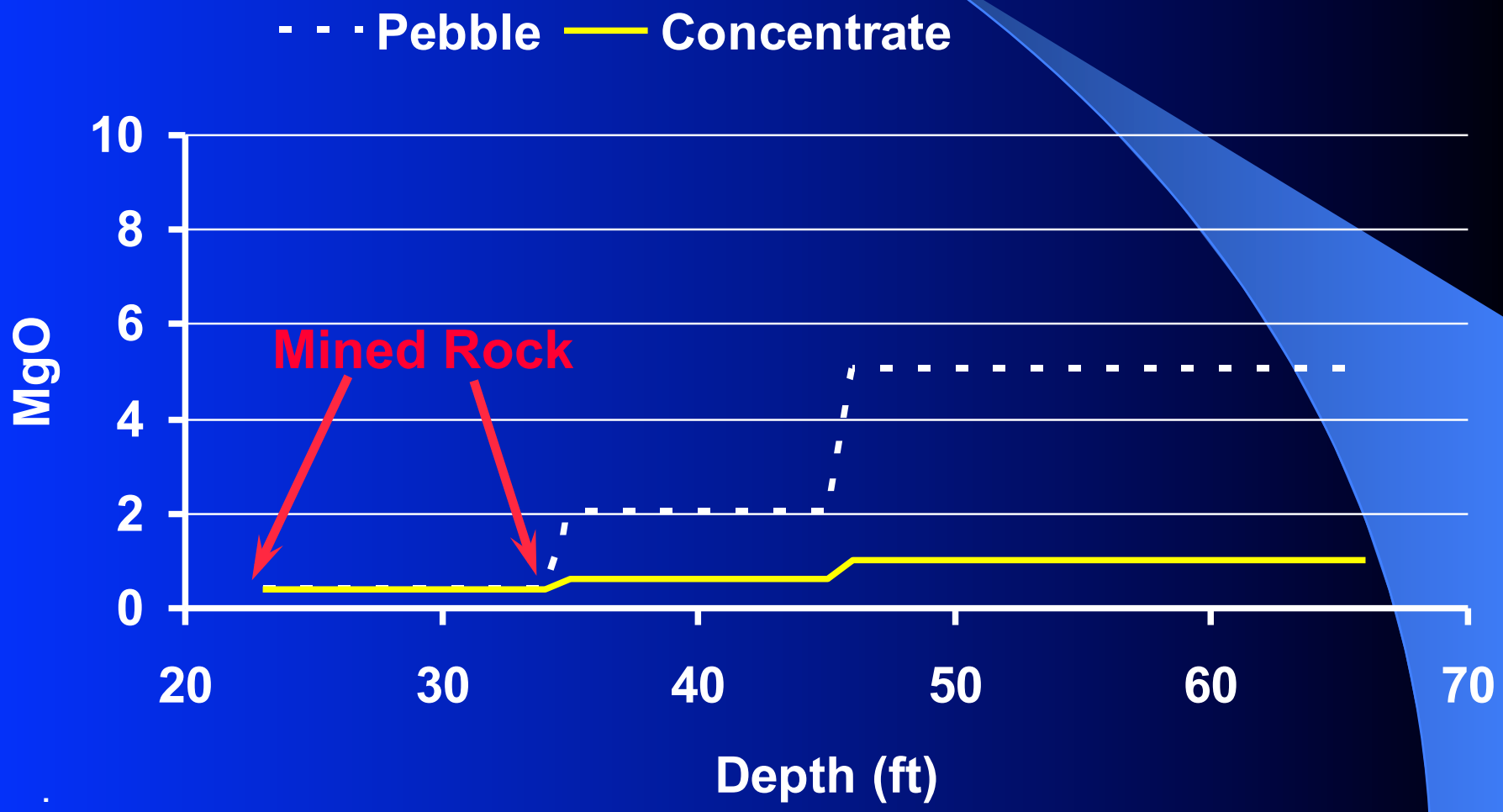
Rock Resource Information

- **Why Not Analyze Cores "Splits" every Foot!!!???**

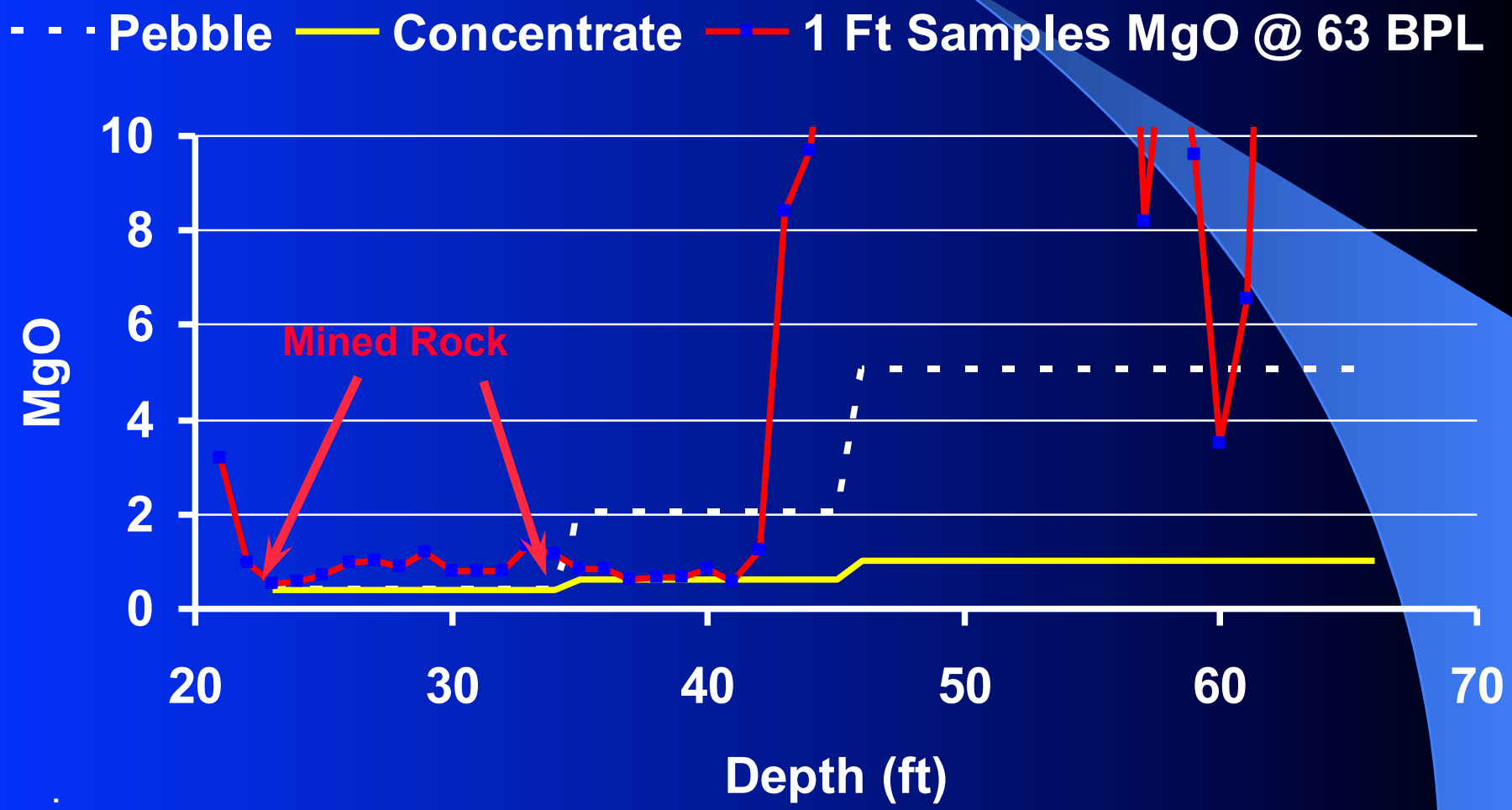
Typical MgO Analysis by Split



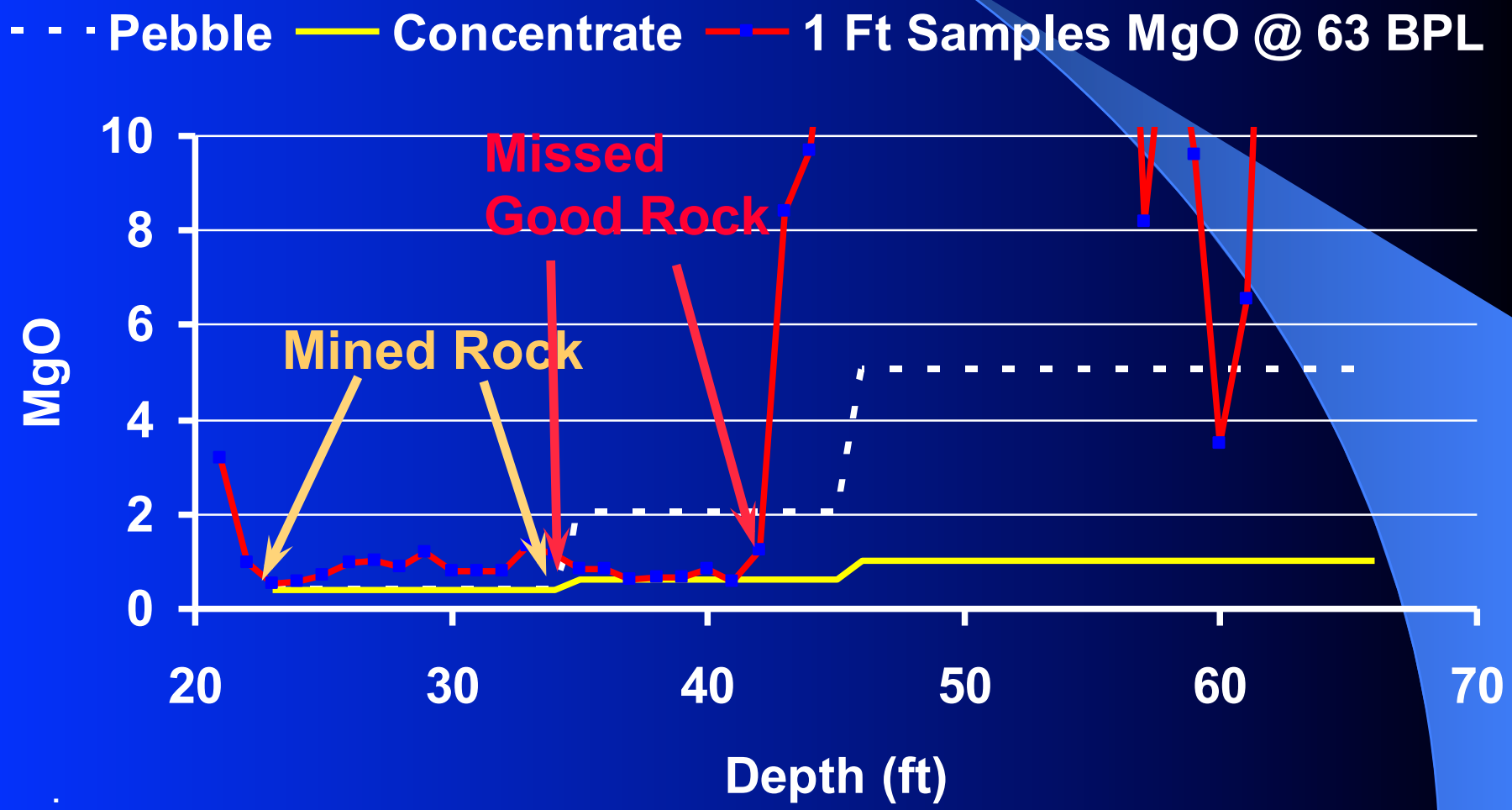
Typical MgO Analysis by Split



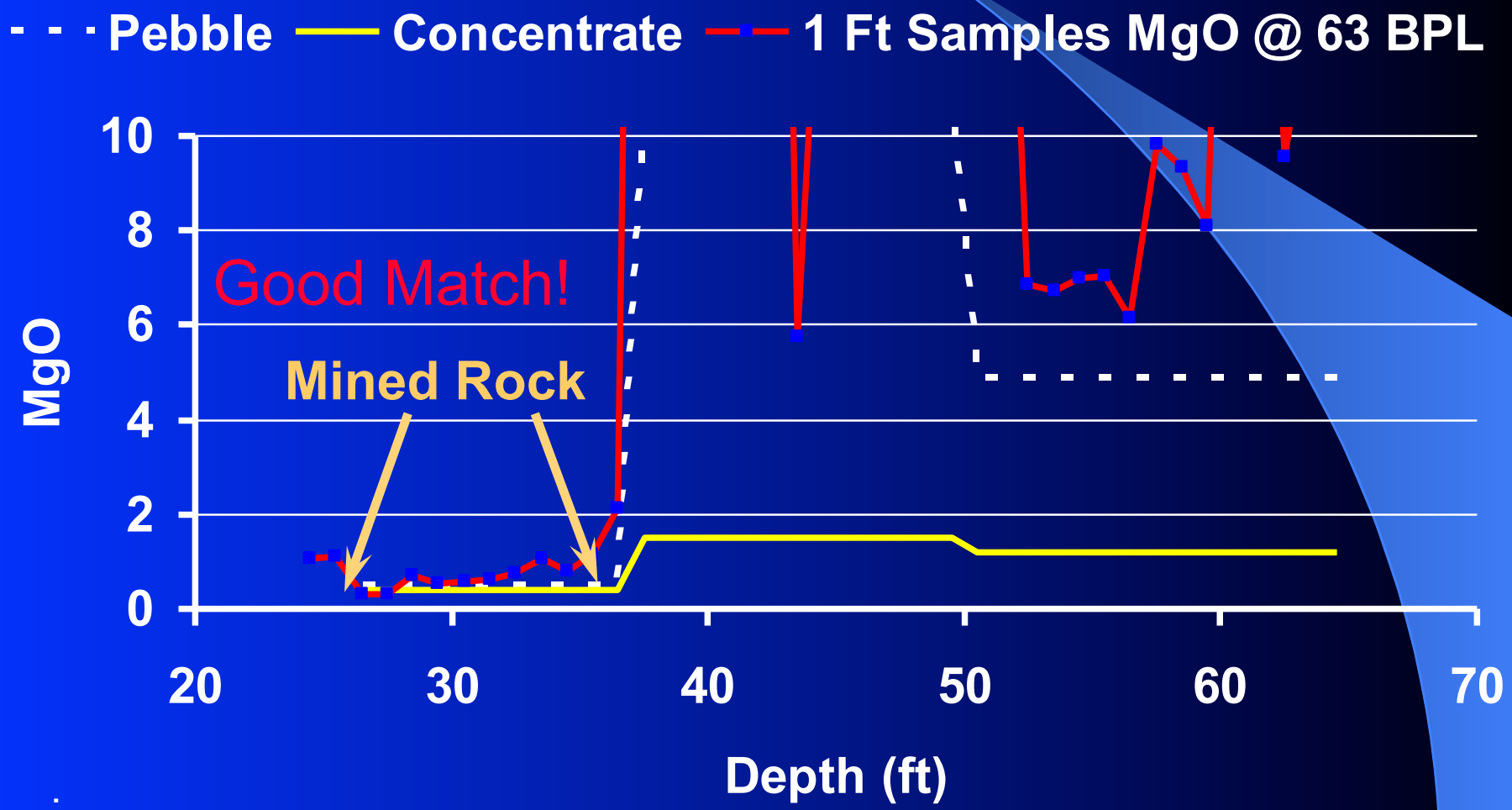
Typical MgO Analysis by Split



Typical MgO Analysis by Split



Typical MgO Analysis by Split



Conclusion

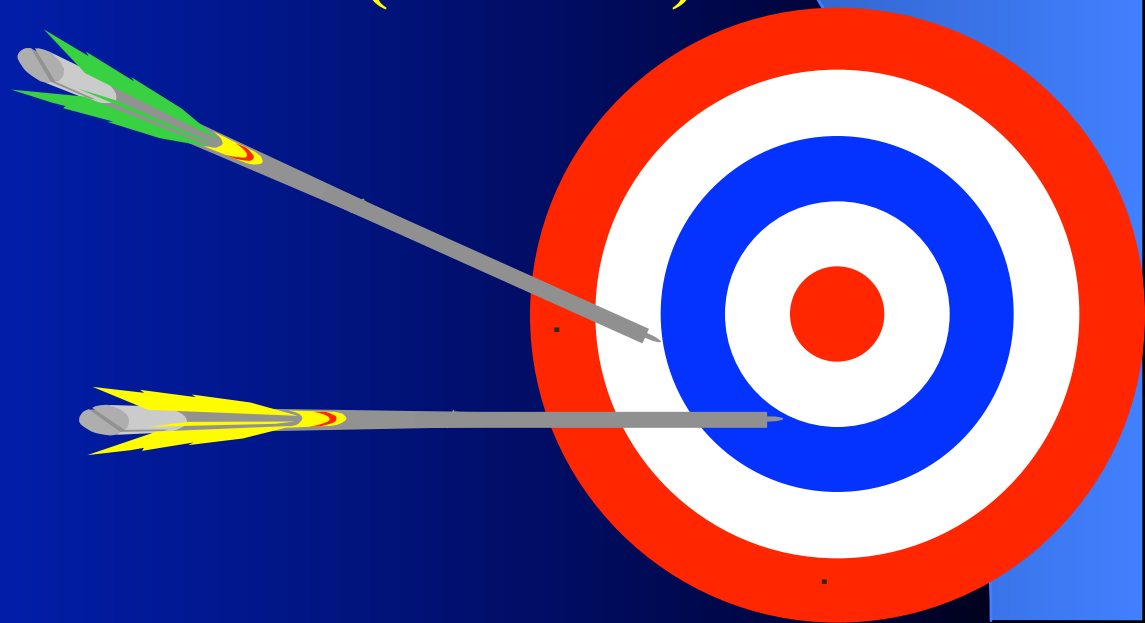
- **Several Hundred Samples Were Taken**
- **There was Good Rock and Bad Rock, No Poor Rock!**
- **Bins of Rock Containing Betwixt 1& 5% MgO Can Only Happen by Blending the Good with the Bad, to get the Ugly**

How Accurately Do We Mine Matrix?

- **56 Samples of "Overburden", "Matrix" and "Bed" Were Collected From 7 Mines**
- **These Were Analyzed Chemically and Physically**
- **Of the 51 Samples That Were Clearly "Mine" or "No Mine", Only 75% Were Correct**

How Accurately Do We Mine Matrix?

- **The Same 56 Samples Were Viewed by 5 Geologists and Characterized as to "Mine" or "No Mine"**
- **Average Accuracy was 79% (73-84%)**



How Accurately Do We Mine Matrix?

- **Both the Dragline Operators and Geologists Were Mining "Matrix" Containing as Low as 2 BPL or With An MgO Over 8%**
- **They Were Leaving Overburden or Bed Containing Over 30 BPL and Less Than 0.2 MgO**
- **It's Not Always Possible to "See" the Difference Between Matrix and Non Matrix**

Additional Information!

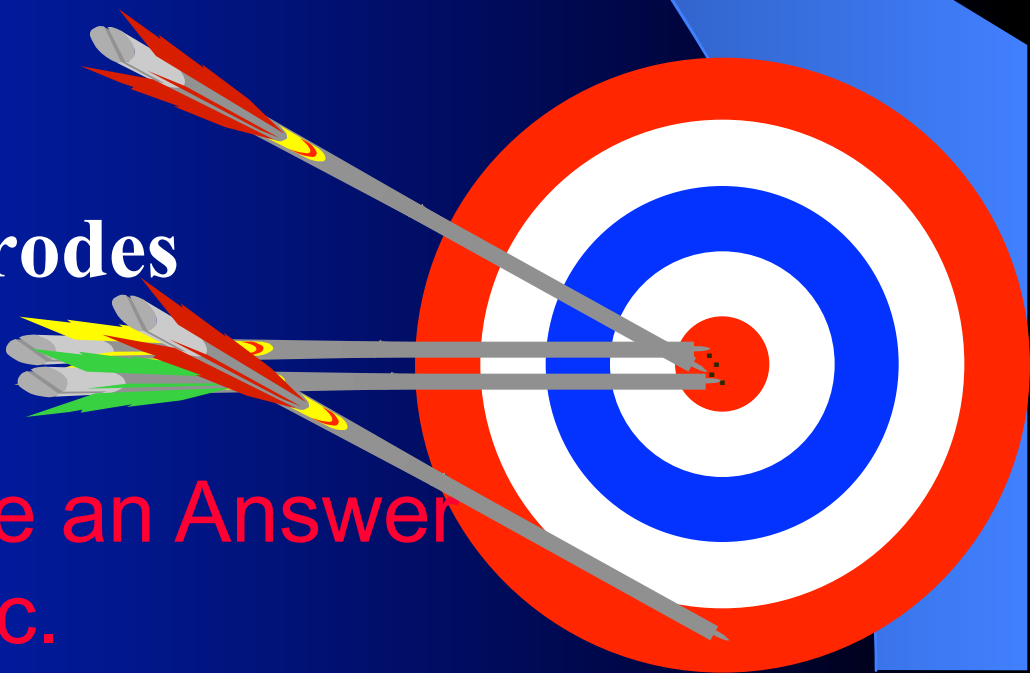
The Impact of "Correct Mining" is at Least 10% More Tons and Improved Quality

What Can We Do About IT?

Mining Technology

- **Conductivity**
- **Image Analysis**
- **Near Infra-Red**
- **Color**
- **Turbidity**
- **Specific Ion Electrodes**
- **Galvanic Couples**
- **Odor**
- **LIBS**

We Need One That is Reliable, Fast, Rugged and Cheap



Can Give an Answer in 10 Sec.

P Efficiency?

- Geology
- **LIBS**

What is the LIBS Technology?

Laser

Induced

Breakdown

Spectroscopy

How Does it Work?

- **High Energy Laser Strikes an Object it Creates a 0.5 cm^3 Ball of Plasma**
- **When the Plasma Cools, it Gives Off a Spectrum**
- **The Intensity of Specific Wavelengths in the Spectrum is Proportional to the Quantity of Each Element Contained in the Object**
- **Some Elements Have Stronger Spectrums than Others (Mg Very Strong, P Very Weak)**
- **In Controlled Conditions, the Analyses Can Have 3 Figure Accuracy**

LIBS

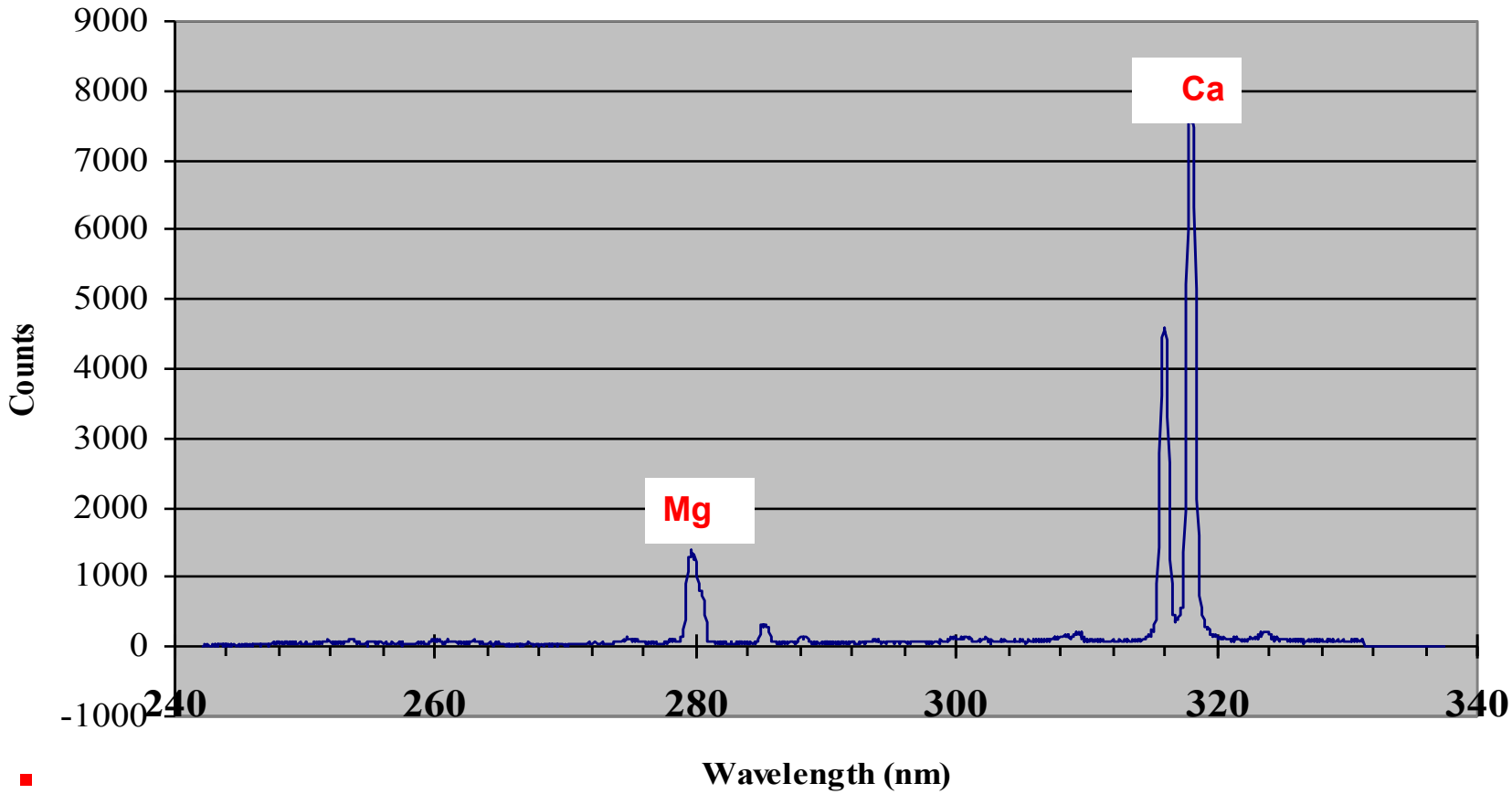
- **Under Controlled Conditions**
  - **A Single Shot Can Tell You if a Rock is Apatite, Dolomite or sand……???**

Apatite

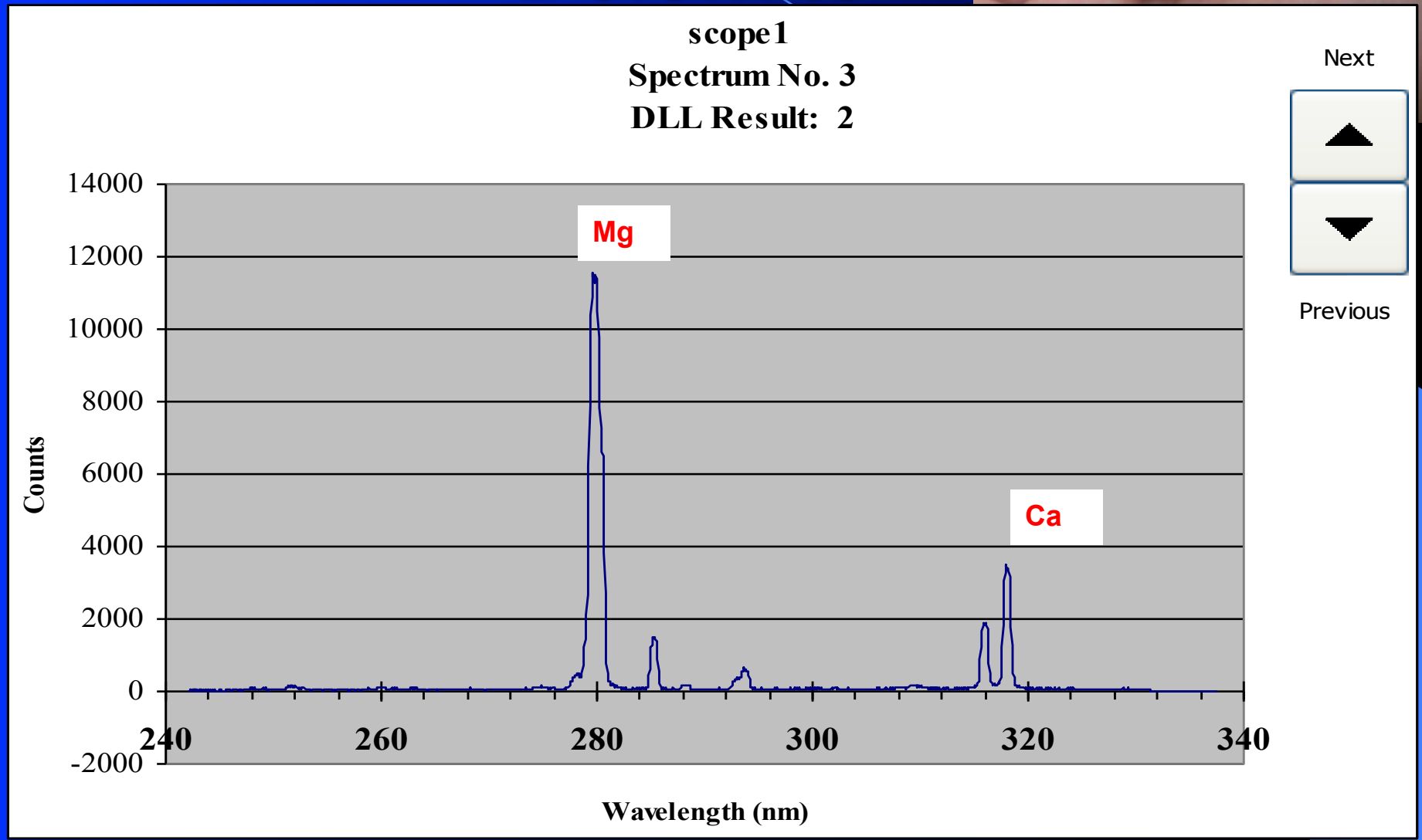
scope1
Spectrum No. 5
DLL Result: 1

Next

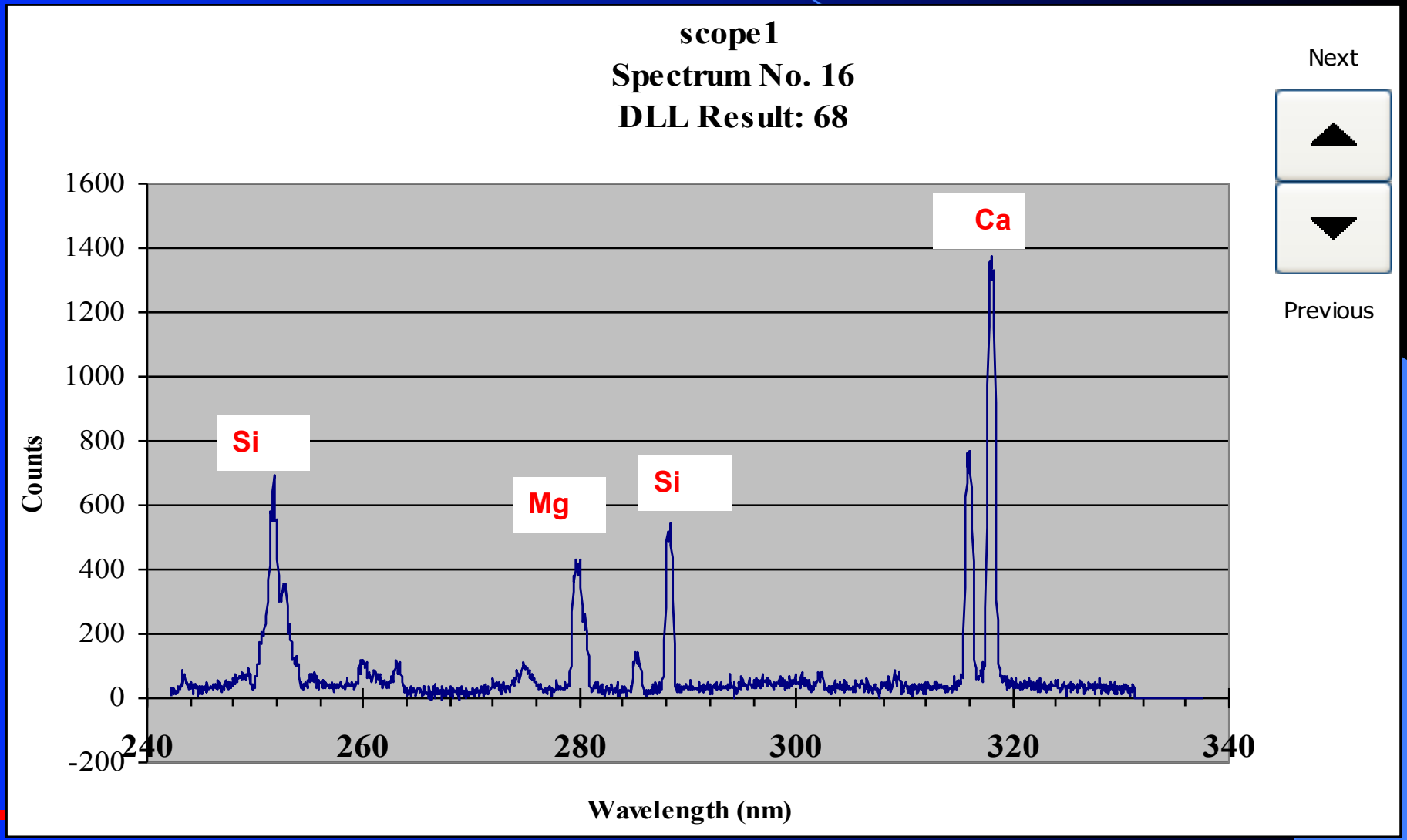
Previous



Dolomite


scope1
Spectrum No. 3
DLL Result: 2
Next
Previous
Mg
Ca
Counts
14000
12000
10000
8000
6000
4000
2000
0
-2000
240
260
280
300
320
340
Wavelength (nm)

Clay


scope1
Spectrum No. 16
DLL Result: 68
Next
Previous
Counts
Wavelength (nm)
Si
Mg
Si
Ca
1600
1400
1200
1000
800
600
400
200
0
-200
240
260
280
300
320
340

Application of LIBS

- **The LIBS Unit Put on Mine Pebble Belt**
- **Rock is –3, +16 mesh**
- **Belt Speed is 10 Feet/Sec**
- **Rock is Wet (15-25% Water)**
- **Rock Level Varied from 1 mm to 140 mm**


LDS
MAR 6 2006

About the Machine

- **Up to 50 mj/Laser Pulse**
- **Up to 20 Pulses (Analyses) per Second**
- **Laser has Life of 30,000,000 Pulses**

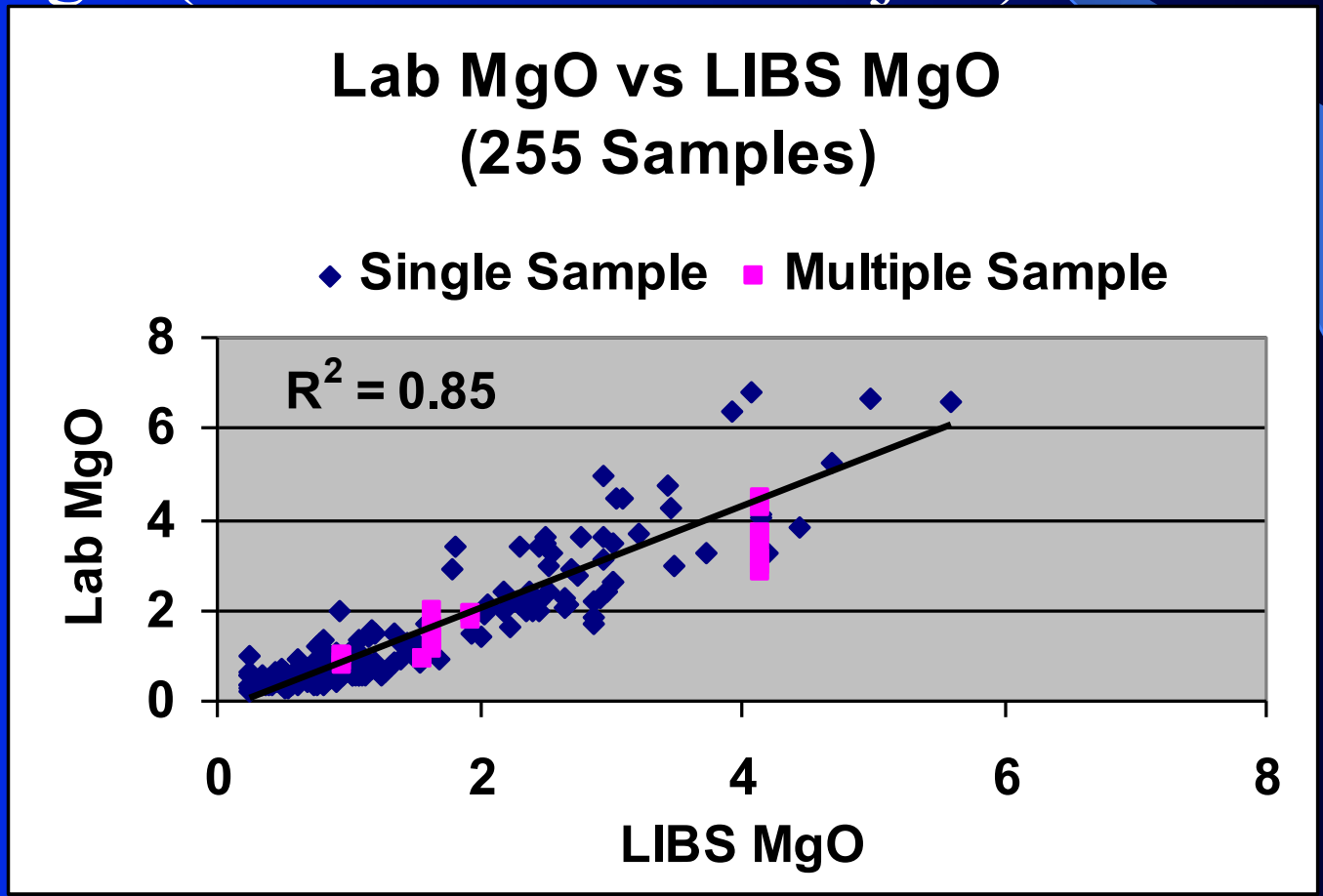
  (35 days of Continuous Use at 10 Pulses per Second)
- **Replacement Laser Costs <$200**
- **(That's < 0.00067 Cents/Analysis)**

About the Machine

- **Output is as %MgO, Al2O3, Fe2O3, Insol, BPL and MER**
- **Machine can be Operated Remotely with Proper Software and Passwords**

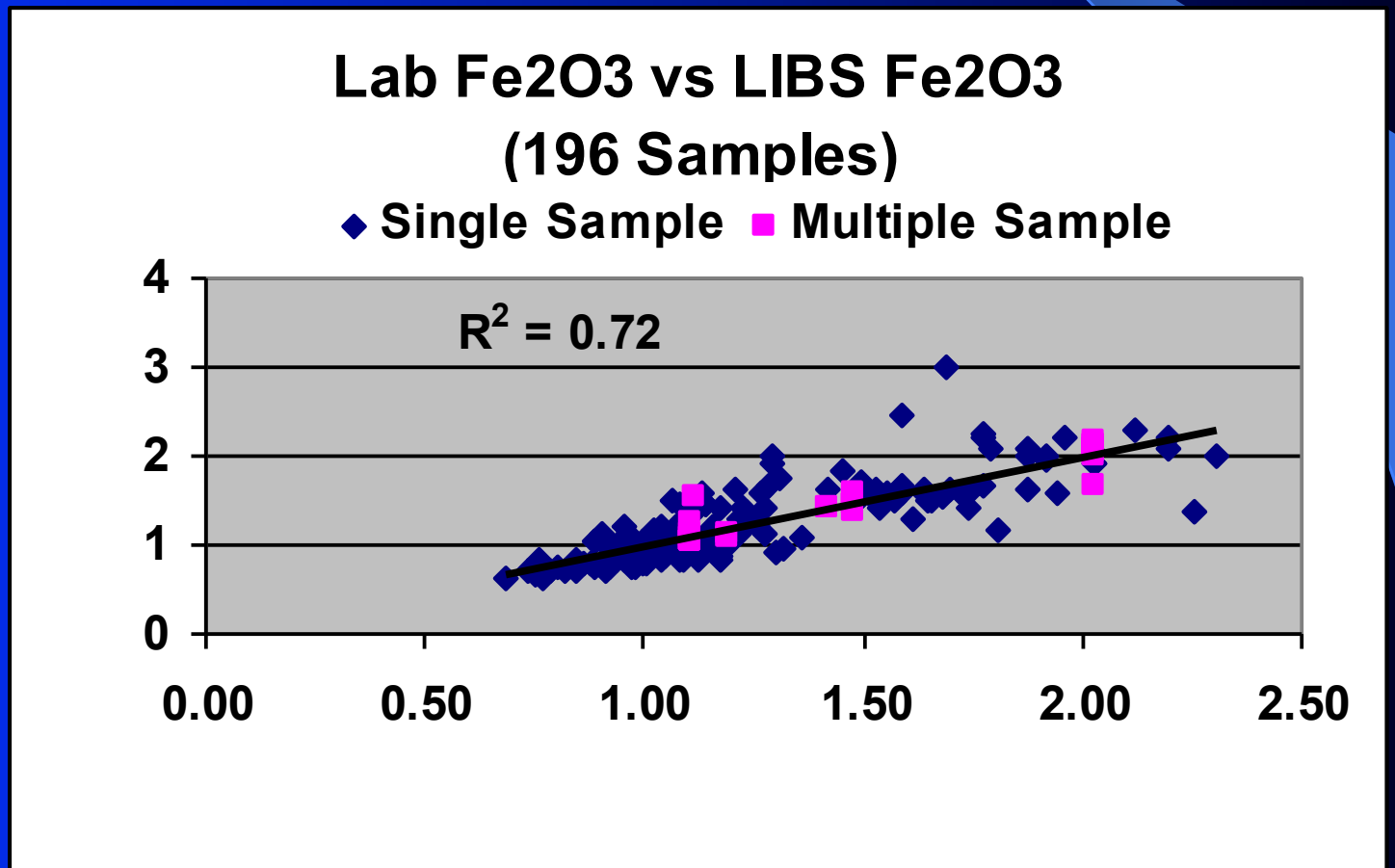
Performance!

- MgO (The Goal of this Project)



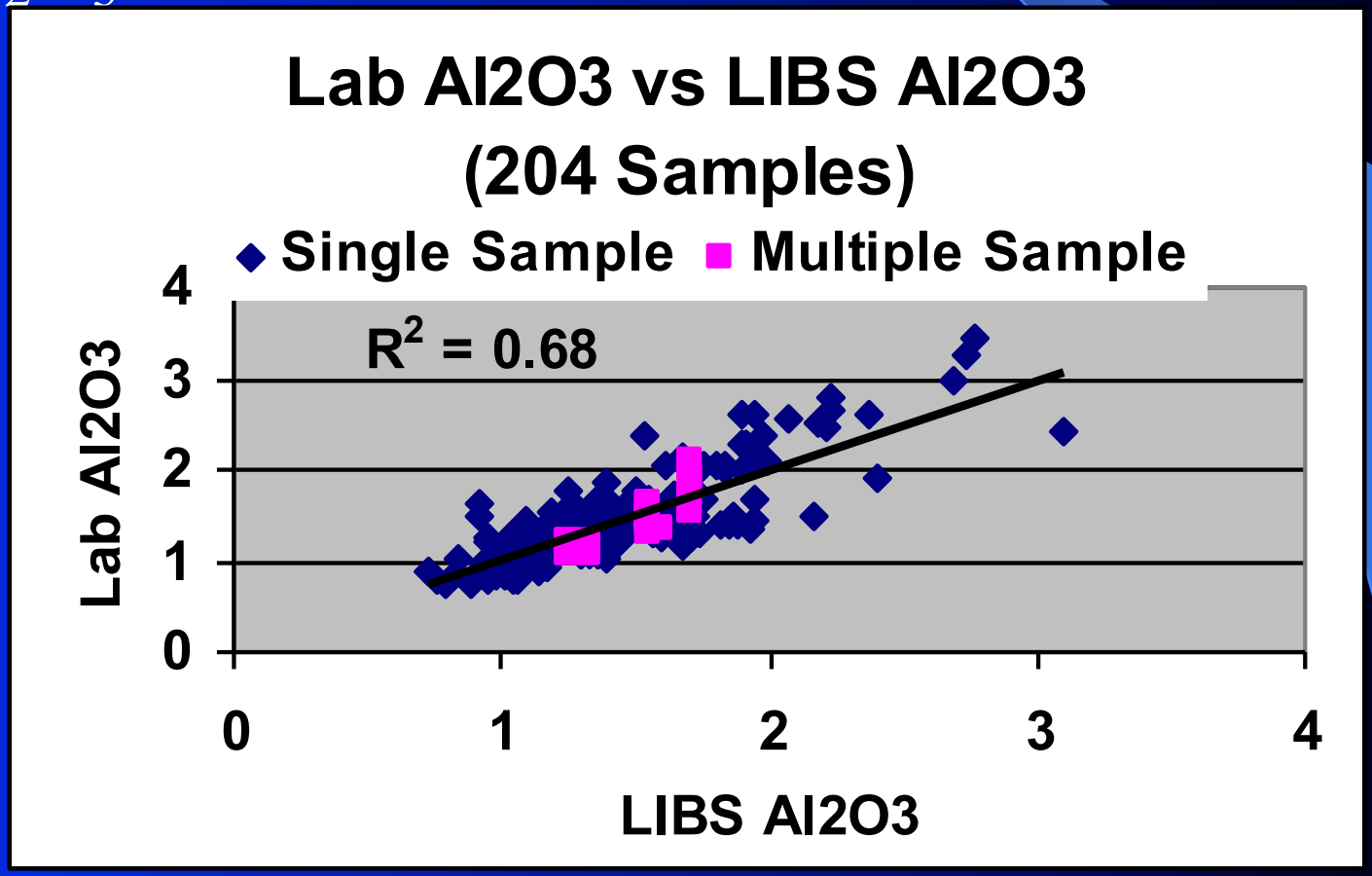
Performance!

- Fe_2O_3



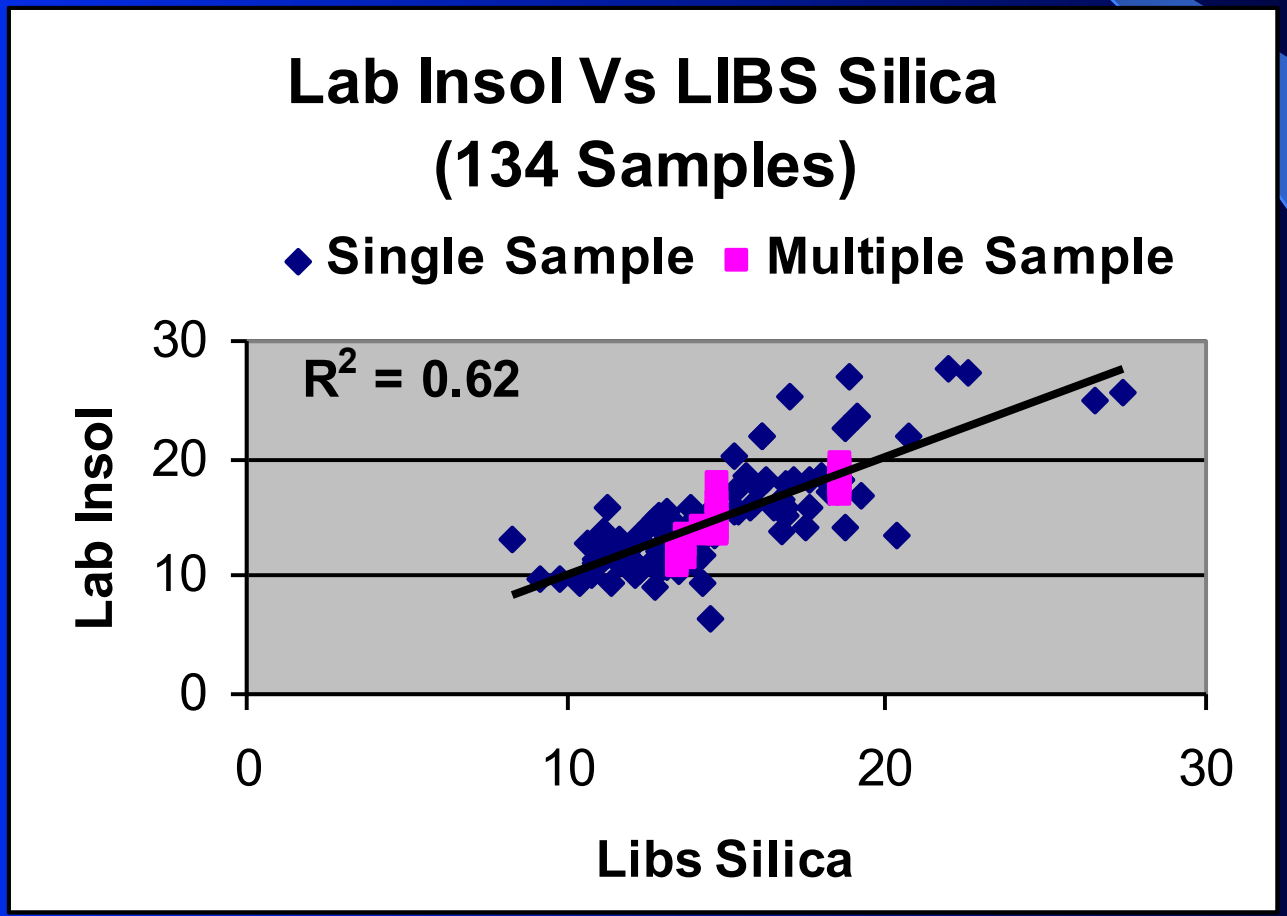
Performance!

- Al_2O_3



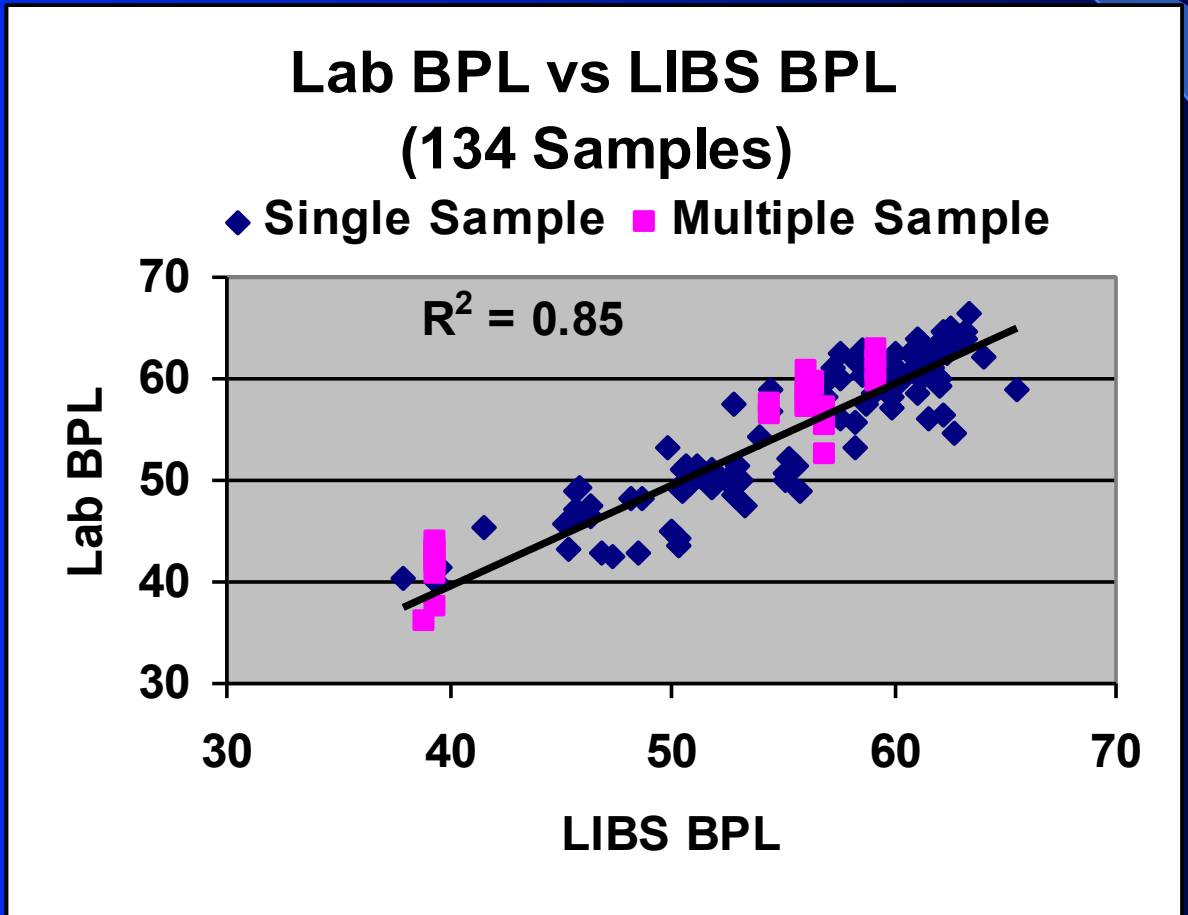
Performance!

- Insol



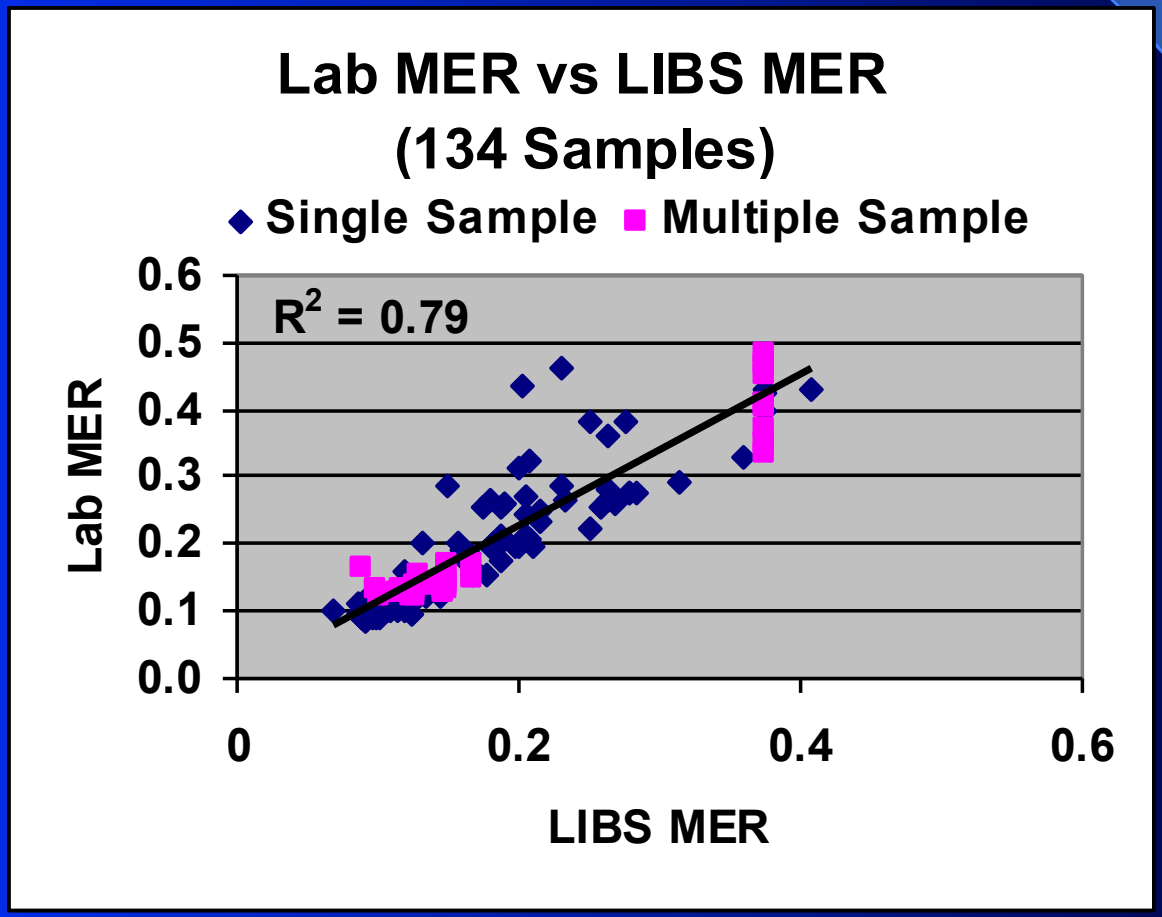
Performance!

- BPL



Performance!

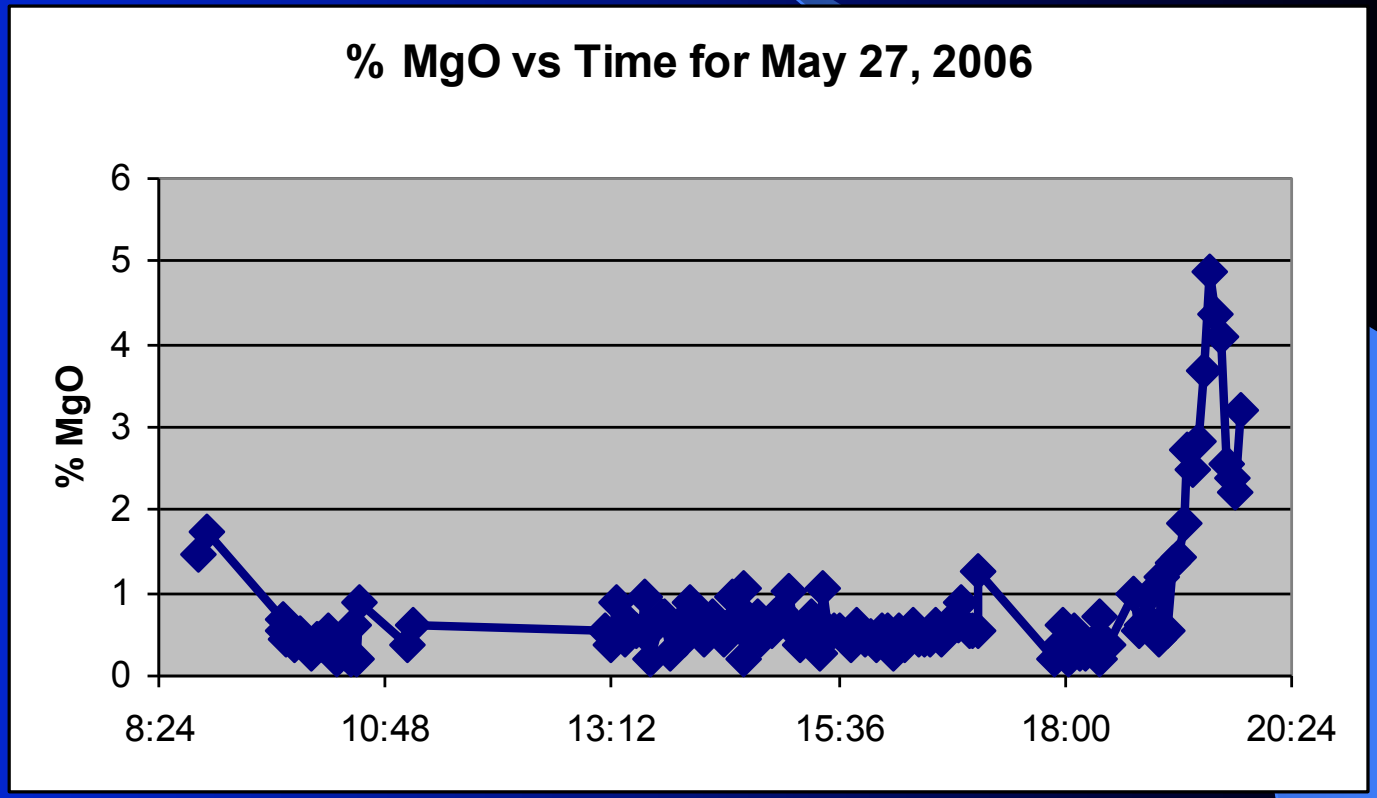
- MER



Field Value

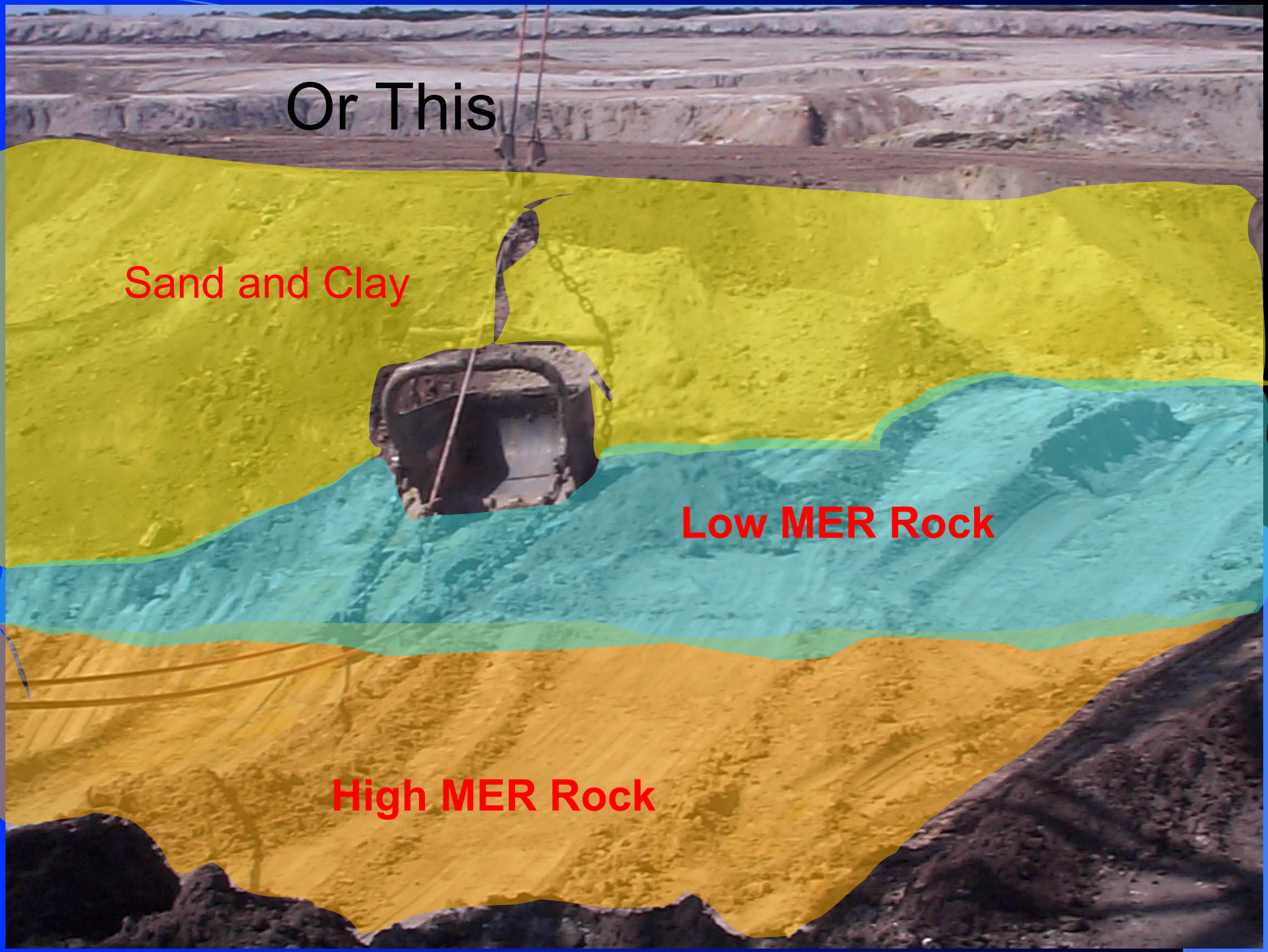
- **If The Pebble Were Discarded During the High MgO Period**
  - **Production Would Have Been Reduced by a Third**
  - **BPL Tons Would Have Been Reduced By Less than 15%**
  - **MgO Would Have Been Reduced From 1.98 to 0.55 (72% Reduction)**
  - **Thus more efficient Phosacid and DAP production**
  - **It's Not a Rare Event!**

Field Value


% MgO vs Time for May 27, 2006
% MgO
6
5
4
3
2
1
0
8:24
10:48
13:12
15:36
18:00
20:24

FIPR has a Current Project to Utilize LIBS at the Mine Cut

- **Would Use LIBS to Analyze Rock in The Dragline Bucket or at the Mine Face**
- **Can Provide Analysis of Materials up to 50 Meters Away**
- **>100 Shots/Second**
- **Would Tell if Material was Overburden, "Good Matrix" or Bed Material**


Or This
Sand and Clay
Low MER Rock
High MER Rock

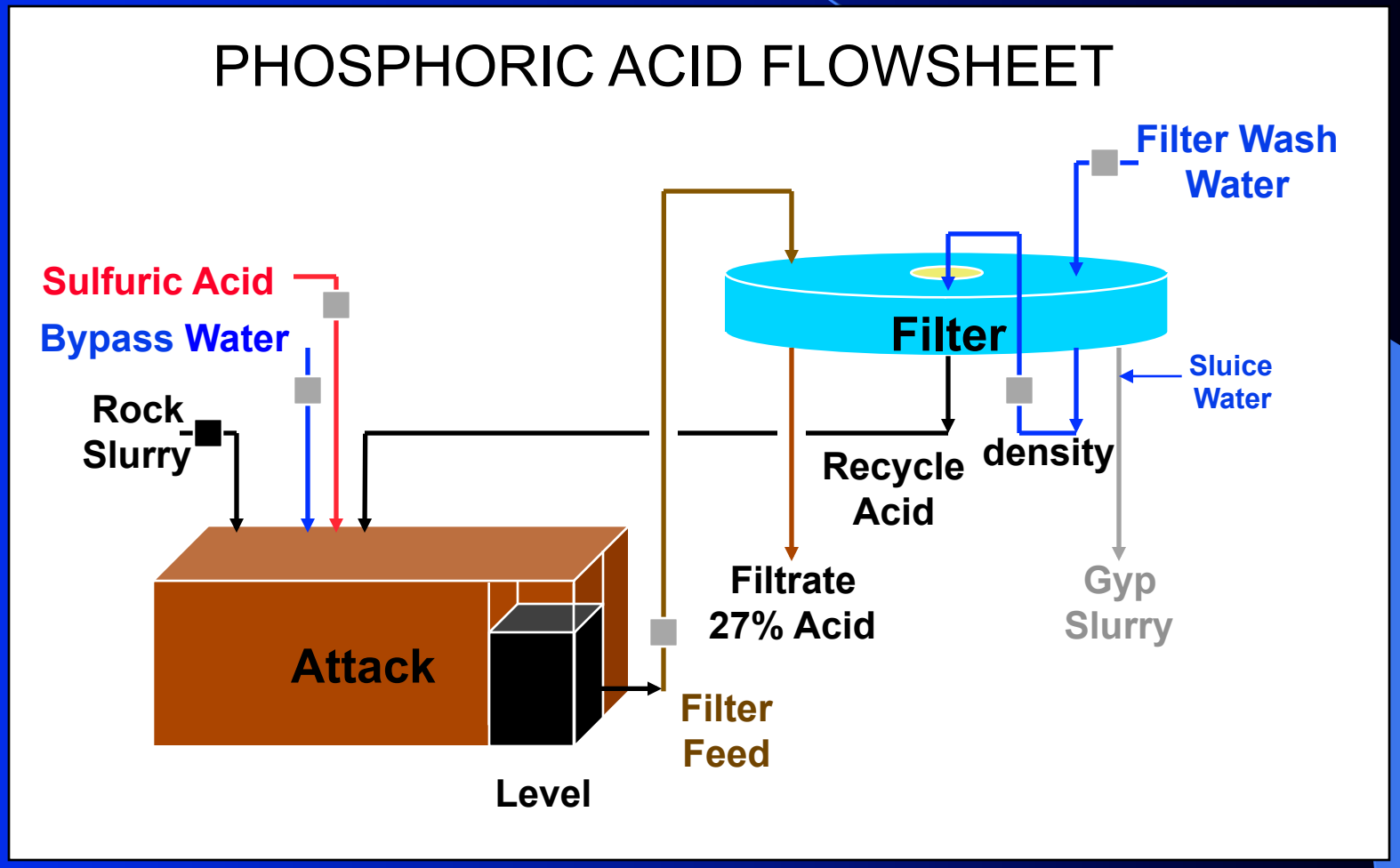
What Has the Industry Done to Improve P Efficiency??

- Don't lose it in the first place
- So Reduce soluble losses
  - Install Phosacid Computer Controls on Phosphoric acid Plants

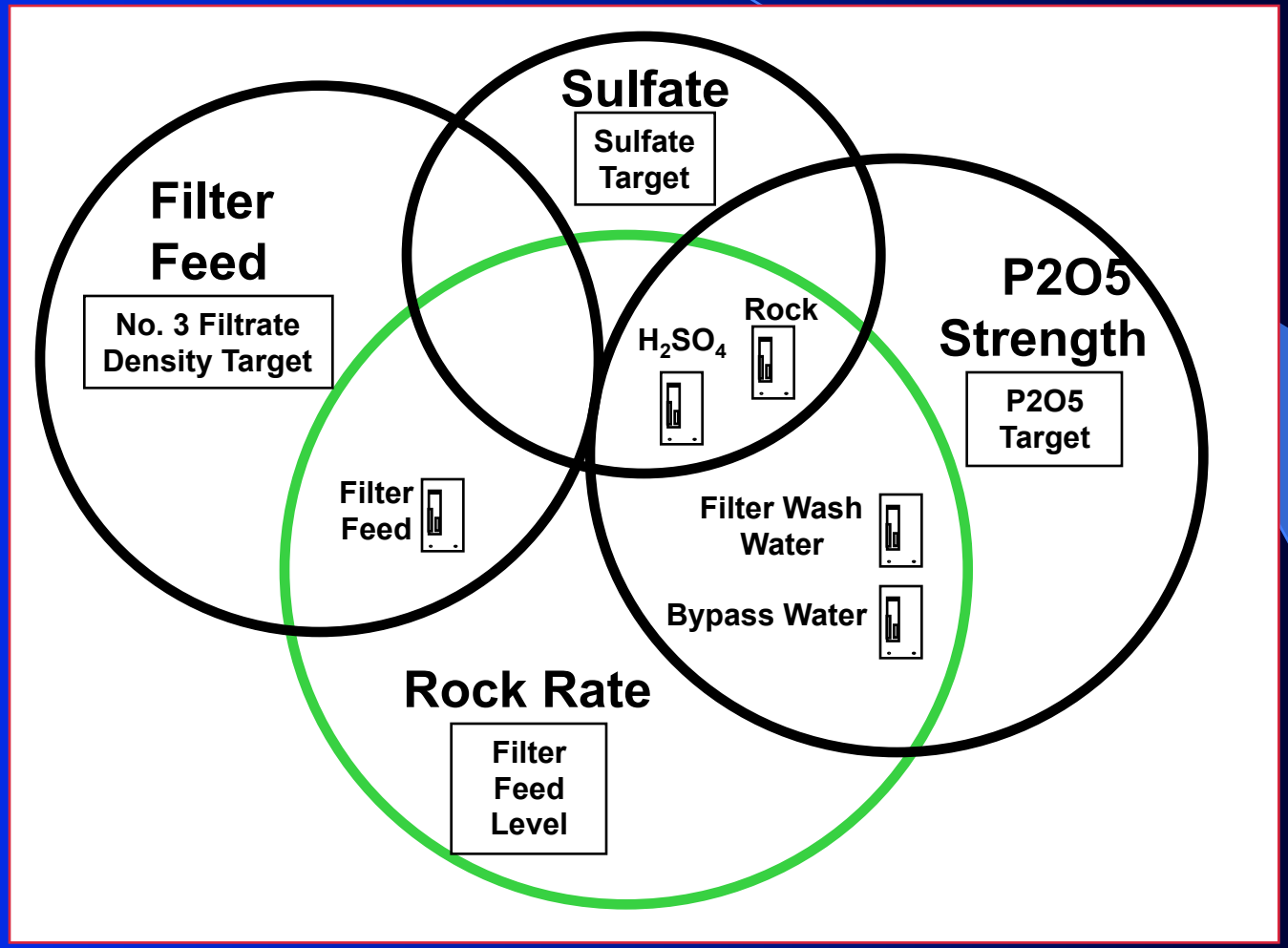
Advanced Computer Controls

- Developed In 1990's.
- Used In All Agrico And IMC Facilities, now Mosaic's.
- Little Or No New Instrumentation Required
- Improves Operational Capacity,
- Increased Filter Recovery.
- Reduced Losses Due To Up-sets
- Reduced Scaling Due To Steady Operation.

PROCESS CONTROLS



The PhosAcid Control Strategies



How Do You Treat/Use Pond Water to Recover P and Reduce Liability?

Recovery of Phosphate Values

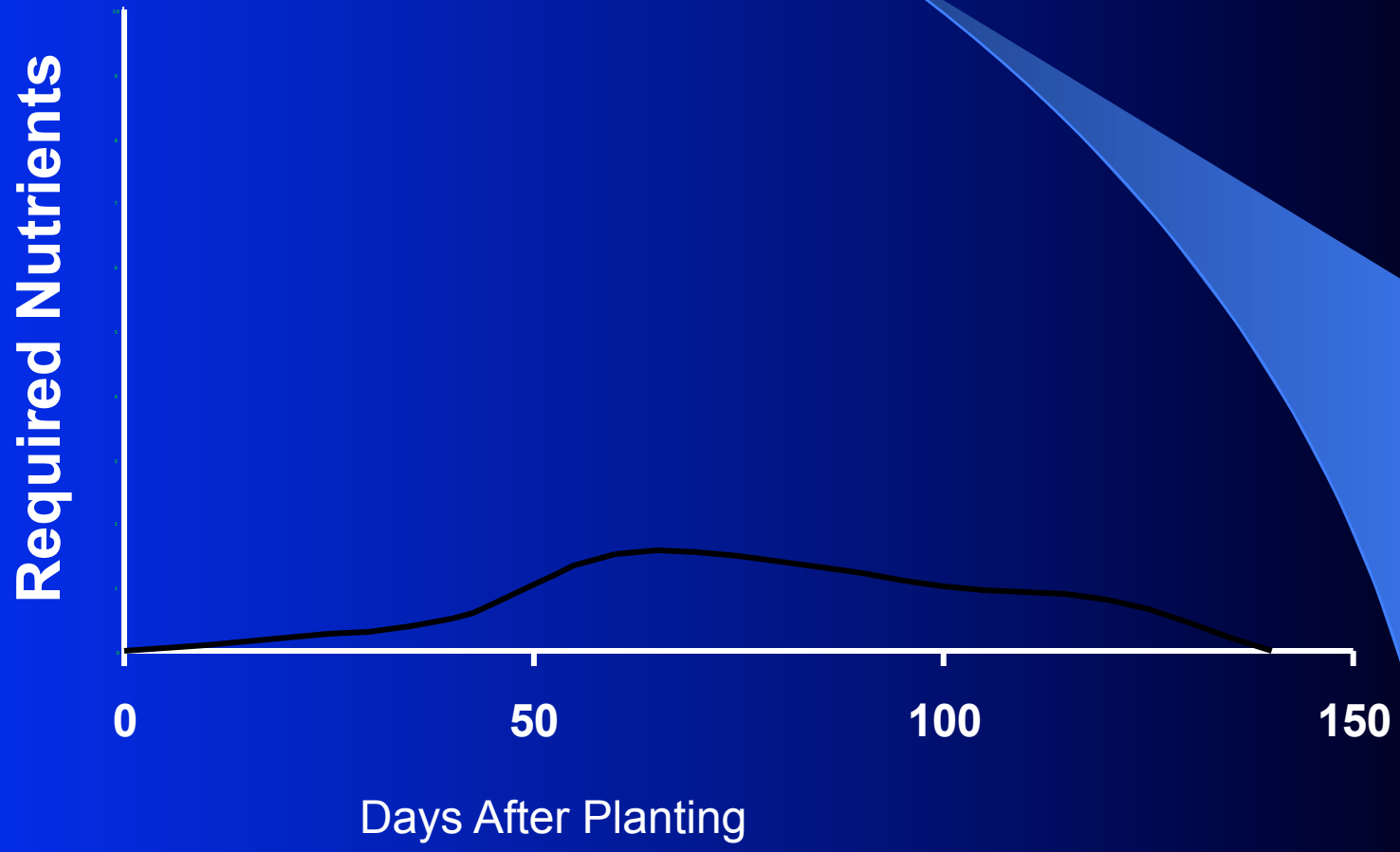
- Recovery Of Concentrate Streams From RO
  - Use In Evaporation And Phosacid Plant
- Recovery Of Struvite
  - Pilot Operations carried out in Florida, Slow Release Fertilizer Produced.
- Recovery Of Di-Calcium Phosphate
  - Bench And Pilot Testing, With Commercial Demonstration In 2008 & 2009 In Florida
  - 8000 tons sold

The Opportunities are Over-Whelming

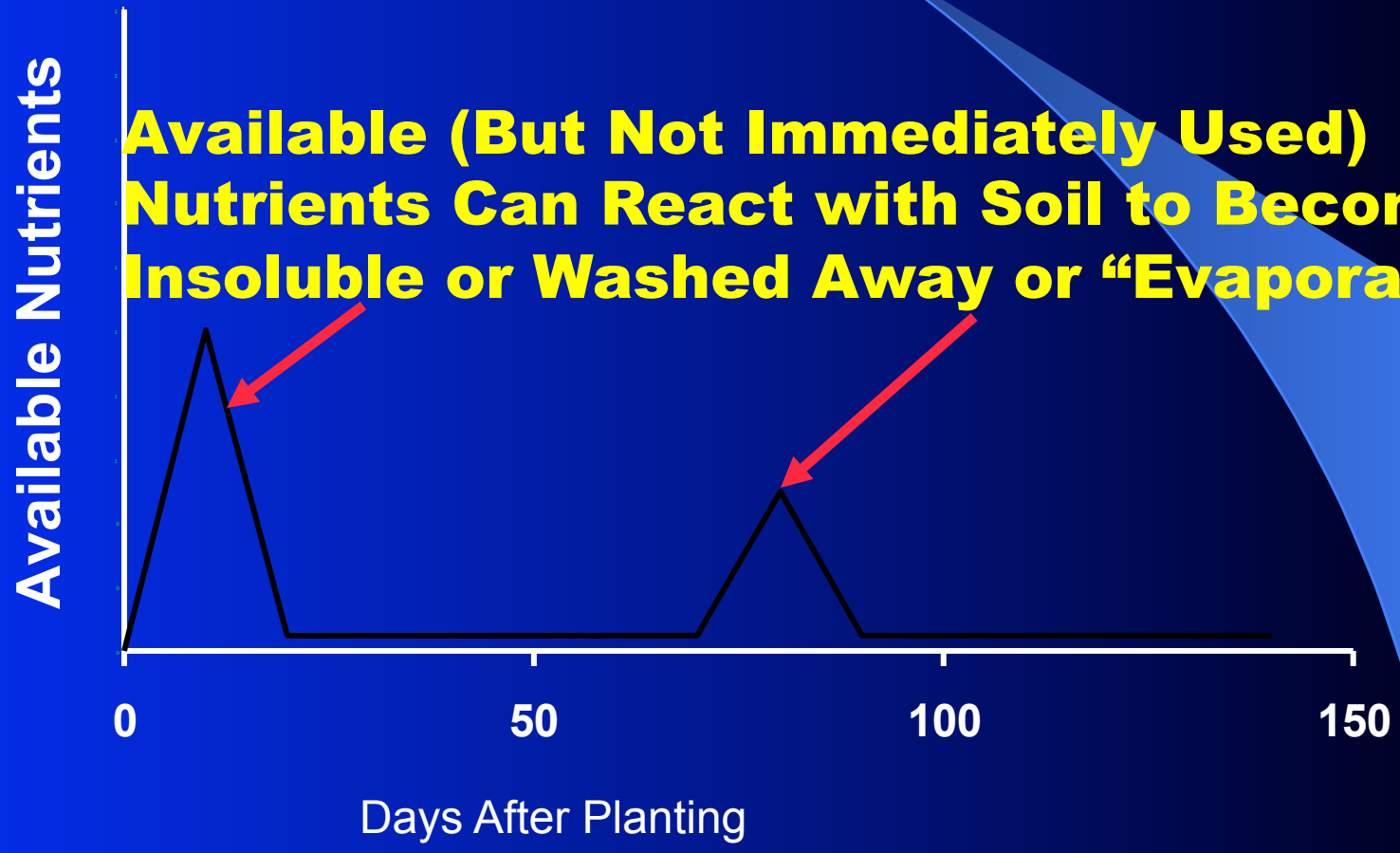
Smart Fertilizer

- **What is Needed to Improve Fertilizer?**
- **We'll Start by Looking at the Forces Affecting the Demand for Fertilizer**

Nutrient Requirement vs Time



Nutrient Availability vs Time



Efficiency is Improved

- **Need Smart Fertilizers That release nutrients when the Plant requires them.**
- **Biological coatings that release nutrients relative to concentration in soil, water availability, temperature, etc., etc.**
- **Bio-Degradable Coatings**
- **Bio-Generation of Keto-Glutonic acids to dissolve rock without sulphuric acid, P in the furrow…i.e. No PG.**

Timeline

- 19th Century
  - Chemistry
- 20th Century
  - Physics
- 21st Century
  - Biology

Smart Plants & Animals

- **In USA 80% Corn and 90% of Soy is GM**
- **New GM stains are increasing N uptake efficiency**
- **Preference for Grass Fed Beef vs. Corn Fed Beef**
  - **Grass fed cows liberate 4 times the methane than corn fed.**
  - **Lignin in grass triggers methane.**
  - **Bio-tech GM Grass reduces Lignin……solves problem**
- **Enviro-pig**
  - **GM Enhanced phytase production, decreases P output by ~60% in manure.**
  - **Seven generation of Porkers still retain P performance**

So If Efficiency is Improved

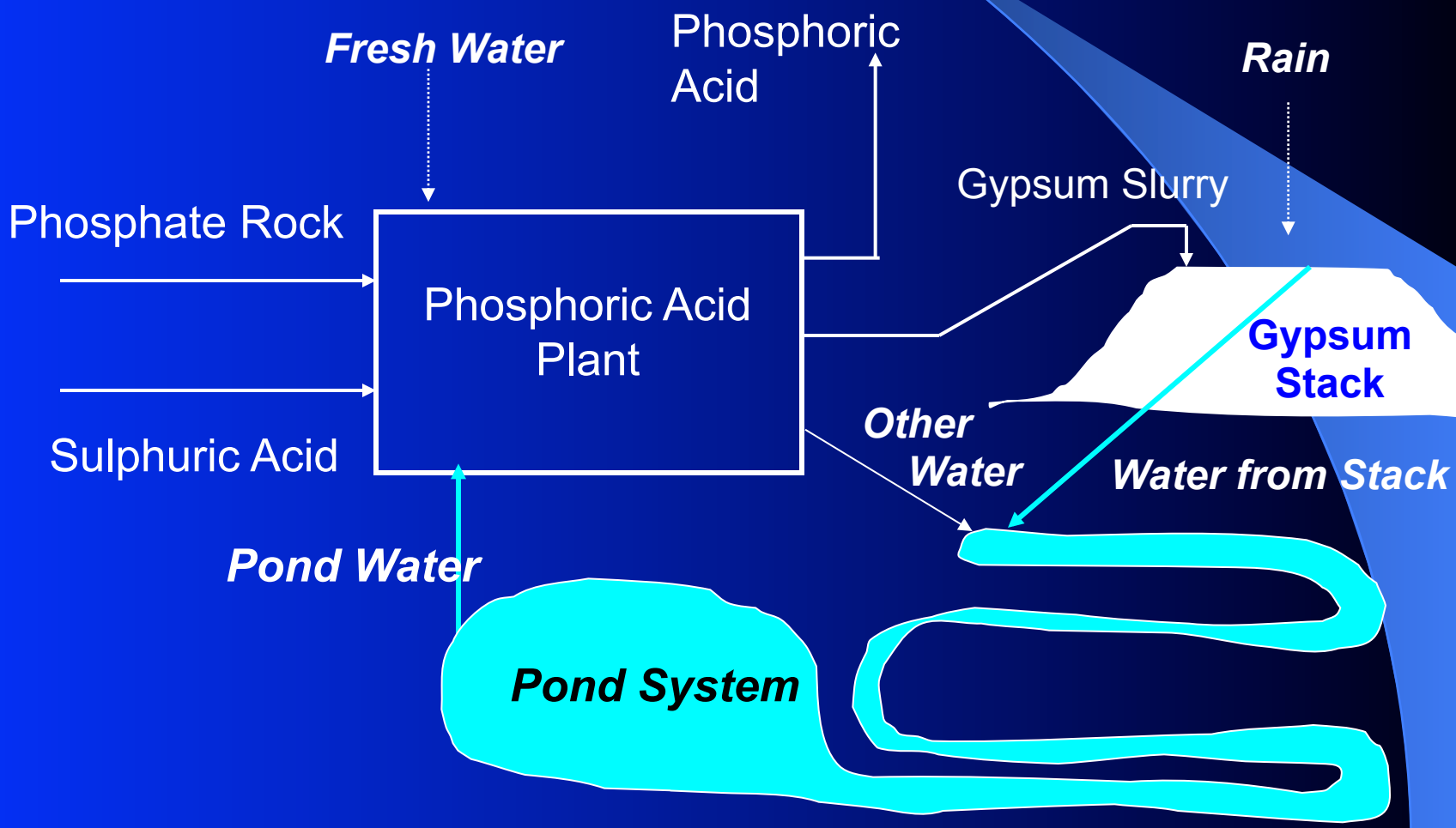
- **Future Demand for Fertilizer Demand Could Drop Very Significantly**

A Cautionary Tale of Unintended Consequences.

What was Phosphogypsum? (PG)

Phosphogypsum, $CaSO_4.2H_2O$ was Produced when Phosphate Rock was Acidulated with Sulphuric Acid and Each Ton of P_2O_5 Generated ~5 Tons of PG.

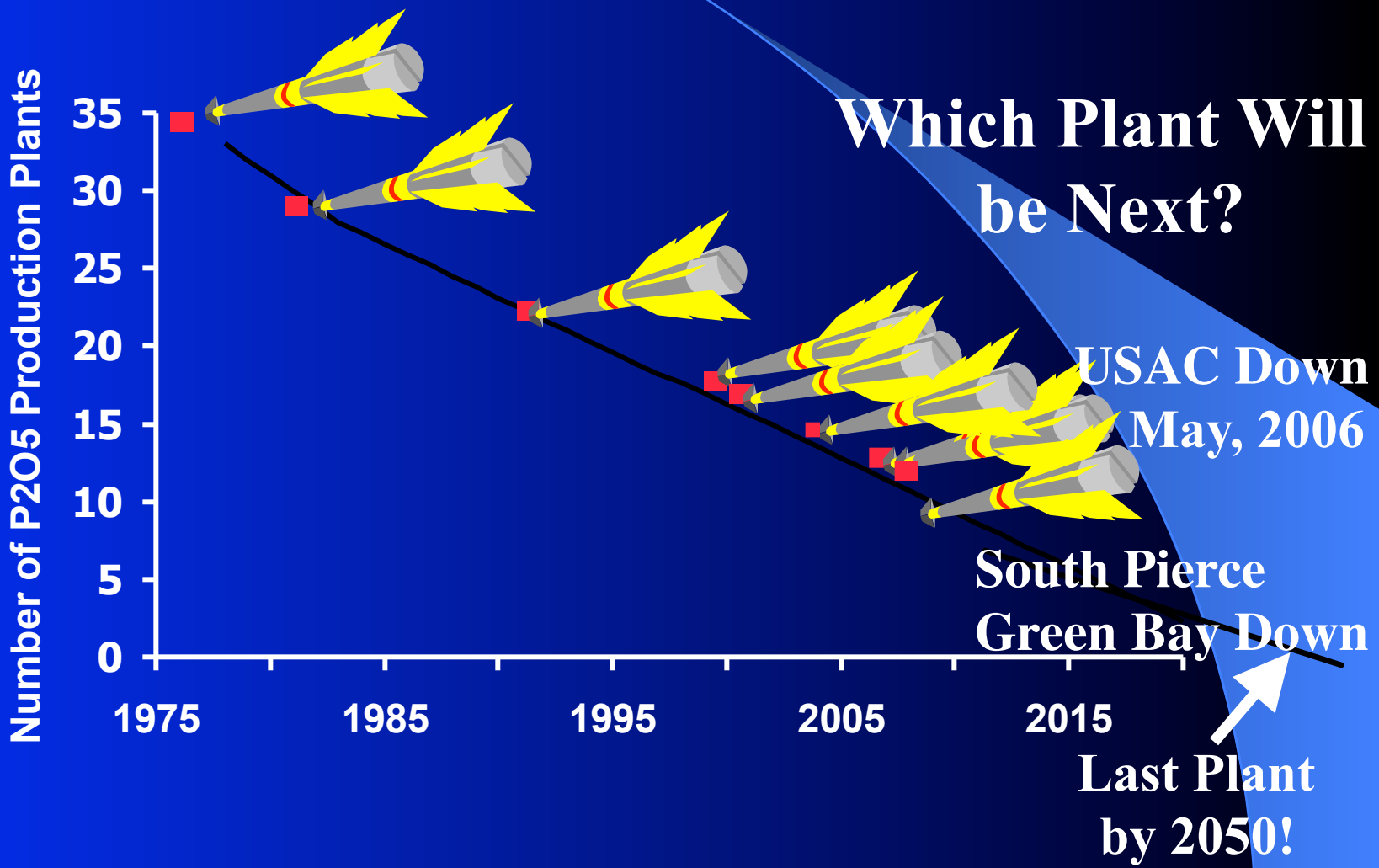
Phosphoric Acid Process
Origin of Pond Water



So How Long Will They Operate?

- **In 1996 a Presentation Entitled “The Bare Bones of the Phosphate Industry” was given at Several Conferences :-**

US Plants and Trends



So Why Will This Happen?

It Was Related to Rising Operational and Liability Costs Related to Phosphogypsum and Pond Water

& Declining Reserves That are Able to be Mined

Self Inflicted Wounds

- 1992 US EPA Promulgated the PG Rule

The Beginning of The End

The Rule

- **The EPA Rule**
- **Sec. 61.204 Distribution and use of phosphogypsum for agricultural purposes. [64 FR 5574 February 3, 1999]**
- Phosphogypsum may be lawfully removed from a stack and distributed in commerce for use in agriculture if **each** of the following requirements is satisfied:
- The owner or operator of the stack from which the phosphogypsum is removed shall determine annually the average radium-226 concentration at the location in the stack from which the phosphogypsum will be removed, as provided by Sec. 61.207.
- The average radium-226 concentration at the location in the stack from which the phosphogypsum will be removed, as determined pursuant to Sec. 61.207, shall not exceed 10 pico-curies per gram (pCi/g) 0.37 Bq/g
- All phosphogypsum distributed in commerce for use pursuant to this section by the owner or operator of a phosphogypsum stack shall be accompanied by a certification document which conforms to the requirements of Sec. 61.208 (a).
- Each distributor, retailer, or reseller who distributes phosphogypsum for use pursuant to this section shall prepare certification documents which conform to the requirements of Sec. 61.208(b).
- Use of phosphogypsum for indoor research and development in a laboratory must comply with Sec. 61.205.

The Rule

10 pico-curies per gram,
0.37 Bequrels per gram

Self Inflicted Wounds

- US EPA Rule defined PG as a “Toxic Waste” with no commercial value, but it was in fact in general commerce
- No Scientific Basis for the Rule
- EPA Could Not Replicate the Data or the Modeling
- So Industry Started to Stack

Regulatory Blight

- **The Stacking of PG Accelerated the Accumulation of Acidic Pond Water, Compounding the Management of the Facilities, and Increased Both Current and Future Financial Liabilities.**

How Much PG Is There in Florida

- 20 stacks
- >1 billion tonnes + of PG, ~35 Million tons per year
- ~25 -45 Billion Gallons (140 Million M^3) of Acidic Pond Water

The Tipping Point

- **What a Situation to Let it Go to Waste and Result in Such Large Closure Costs and Liabilities.?**
- **In 2001 The Piney Point Facility Was Dumped on the State of Florida.**

The US EPA Effect
Unintended Consequences

- Was the Rule the Solution or the Problem?

The End

but

Waste or Resource
"Stack Free By 53"

- **Objective**
  - **Find a Viable Economic and Environmentally Acceptable Alternative to Stacking Gypsum**
- **FIPR Funded a Project on PG Use**

www.stackfree.com

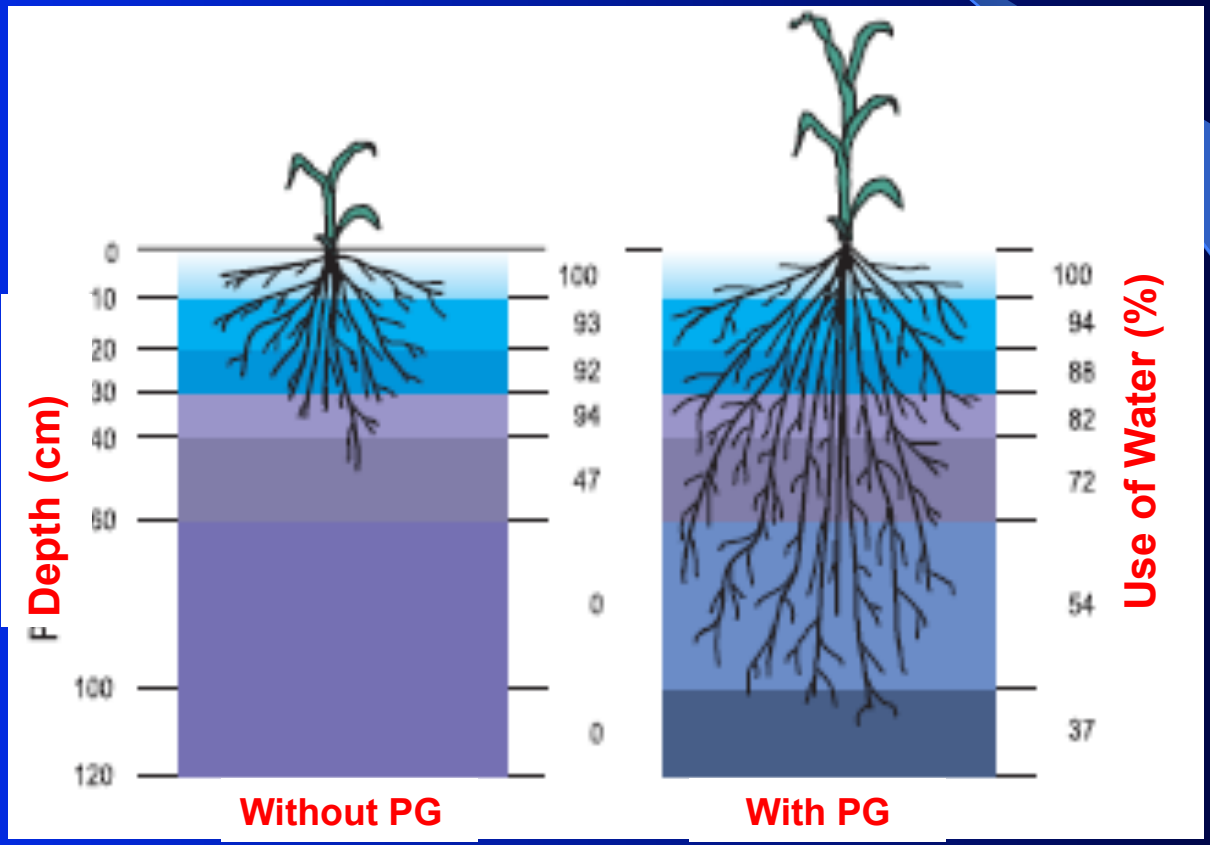
A New Perspective

- An extensive Literature Search Found:-
- Over 50 Beneficial Uses of PG.
  - Agricultural Uses
    - Over 60 Crops
    - Application Rates are Typically 100-200 lb/Acre, 125-250 Kg/Ha, but in Some Cases >2000 lb/Acre, or 2.5 Tonne /Ha

Agriculture

- Need for Calcium and Sulfate Values
- Treatment/Reclamation of Sodic Soils or Soils with High Aluminum
- Lack of Soil Sulphate Due to Less Acid Rain
- Increased Land Salinity Due to Irrigation and Fertilizer Application.
- Increased Water Permeability/Reduced Runoff

Effects of PG on the roots



Pasture Grass

- Pasture Grass Covers 8.7 Billion Acres or 3.5 Billion Hectares
- Even at an Application Rate of 0.05 Ton/ Yr/Acre (0.12 Tonne /Yr/Hectare), it Would only Require 45% of Worlds Pasture Grass to Consume 160 Million Tons/Yr of PG
- Benefits are 20% Increase in Grass Yield and Reduced Water Runoff (Pollution)

IAEA STUDY

IAEA Has Determined that Norm materials do not pose any harm and do not require regulatory controls under 1 Bq/g

Thus most Florida and World PG can be used in Agriculture.

Many Nations have accepted this 1 Bq/g Value

We Need to get EPA to Move Now.

(Good Luck!!!)

The End of the Beginning


RANDON

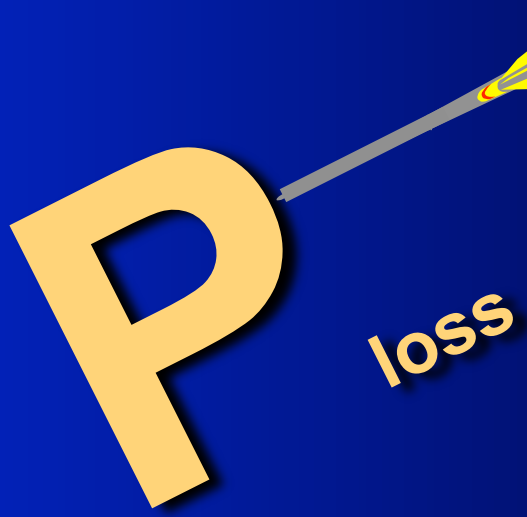
P_{loss}

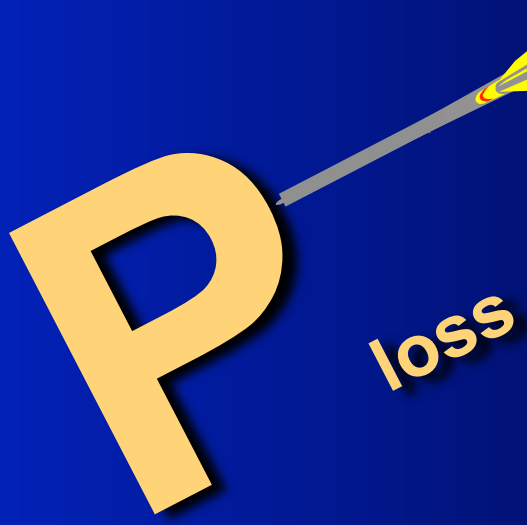

P
loss


P
loss


P
loss


P
loss


P
loss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The Small Print

Phosphogypsum or any component is contraindicated in those hypersensitive to use of waste products, particularly if you have high blood pressure, and if employed by an industrial conglomerate in a legal capacity. The use of phosphogypsum as an embalming aid is strictly prohibited. Do not use if you are pregnant as it is too late. The disposal of relatives in PG stacks is also frowned upon, particularly near inhabited areas. Excessive dosages can result in tall buildings falling down, or leaning at precarious angles. Extreme dosage in agricultural pasture application are reported to cause cows to cough, and liberal applications of Robitussin-cow is appropriate. Houses may be built on roads made with phosphogypsum, provided that occupation is limited to 24 hours per day, on alternate Thursdays, especially in New York. For airplane runways it is very important to adequately level the phosphogypsum.

Otherwise phosphogypsum can be used to no ill effect, particularly in agricultural and construction activities.

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