Chilean Mill uses PeCOD® COD Analyzer for Determination of Chemical Oxygen Demand (COD) for Savings in Bleaching Process

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Facts on the Chilean Mill

- Global company that produces many types of wood products
- Produces pulp used for:
  - Paper
  - Packaging material
  - Diapers
- Produces board and wood used for:
  - Furniture
  - Construction

What is COD and How is it Significant to the Bleaching Process?

- COD is Chemical Oxygen Demand
- COD is the amount of oxygen required to fully oxidize organic matter
  - It is used as a measurement of the oxygen-depletion capacity of a sample contaminated with organic waste
- It is significant to the bleaching process because it impacts the required chemical dosage of chlorine dioxide (ClO_2) used for pulp bleaching
- Higher COD concentrations can result in greater consumption of ClO_2, which means excess bleaching chemical must be added to the process to compensate for the loss

Traditional Method for Determining COD

- Traditional method for measuring COD in the wash water was by SCAN-C 45:00 (SCAN method)
- The SCAN method is used for measuring the washing efficiency of the process
- The final equation calculates COD removal by washing in units of kg per ton oven dried pulp
- The test involves sample collection, COD analysis, and sample drying
- COD of the wash water is measured by dichromate method (~3hrs)
- Sample drying ~4hrs
- Total time of the test = ~ 7 hours

Pulp Washing and Bleaching Challenges

- Experiencing deficiency in pulp washing
- Current SCAN method for determining COD removal during washing takes too long
- Results aren’t timely for operation control
- Improper ClO_2 dosing:
  - Excess bleaching chemicals are used from accidental over-dosing, or to compensate for higher COD concentrations

Pulp Washing and Bleaching Challenges Cont'd

- COD concentration in the delignification stage (pre-bleaching) must be less than 12 kg COD/dry ton
- Knowing the deviations of the organic load in the process would allow operators to adjust ClO_2 dosages, reducing excess chemical consumption, which is key to the profitability of the process

Objectives and Goals to Improve the Bleaching Process

- Objective:
  - Reduce the COD analysis time in the pulping process, to deliver a timely result to operations, thereby avoiding excess consumption of ClO_2
- Goal:
  - Decrease analysis time by 90%, to allow operators to respond to process deviations

Mill Uses PeCOD® COD Analyzer for Fast COD Analysis

- Implementation in the lab:
  - Validated the new method with respect to the standard SCAN method
- Implementation into operations:
  - Faster COD results lead to closer monitoring of the wash area and improved bleaching process control

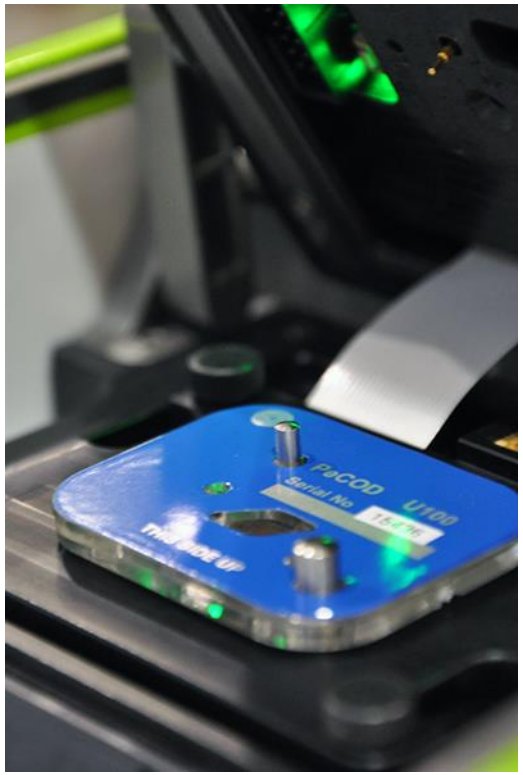
What is the PeCOD® COD Analyzer?

- A patented technology that measures COD by oxidizing organic matter by photoelectric method
- peCOD method eliminates the use of **mercury and potassium dichromate**
- Safe for both the environment and the analyst
- Results in less than 15 minutes
- Accurate method with a detection limit of 0.7 mg/L, and upper range of 15,000 mg/L

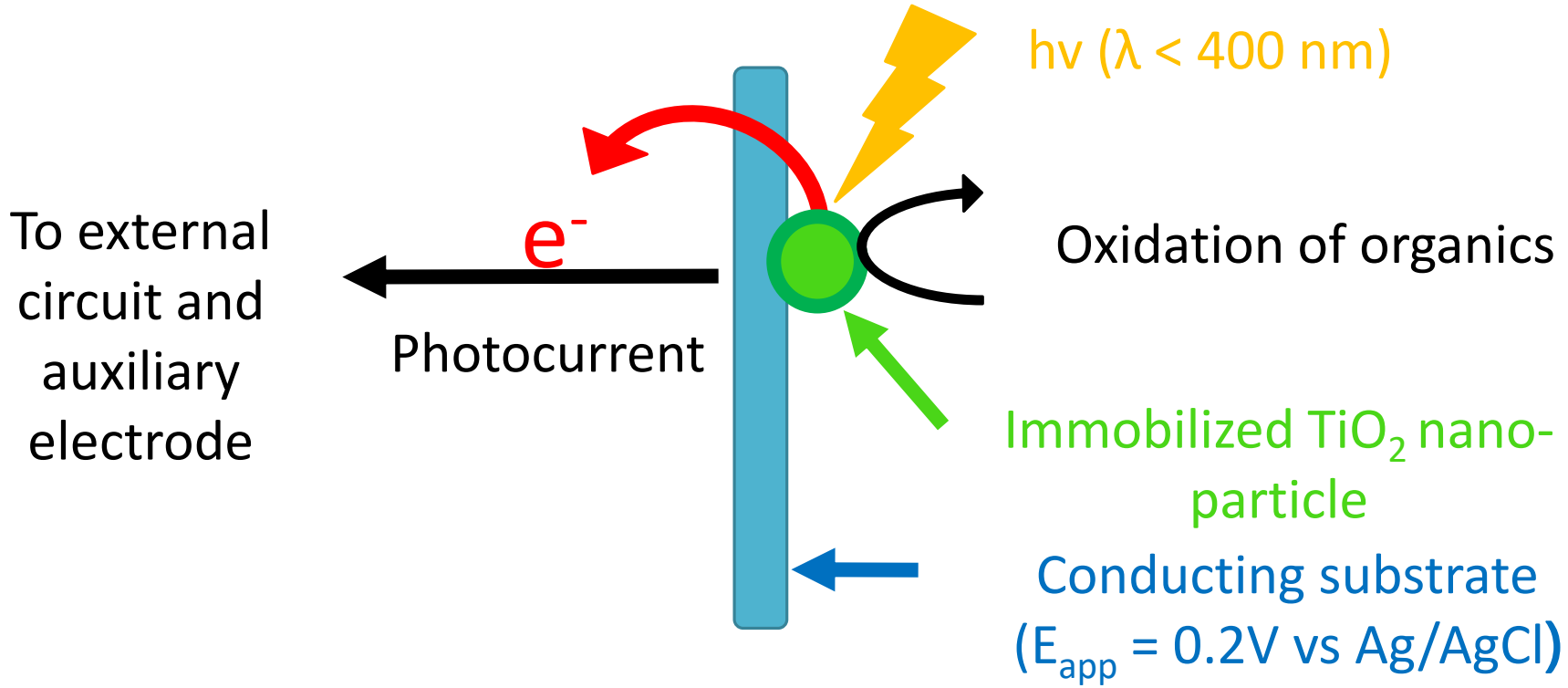
Nanotechnology

- The core of the technology is the PeCOD sensor, which consists of a UV-activated nanoparticle titanium dioxide (TiO_2) photocatalyst coupled to an external circuit

- The powerful oxidizing potential of UV-illuminated TiO2 ensures that virtually all species will be fully oxidized giving a true measure of COD

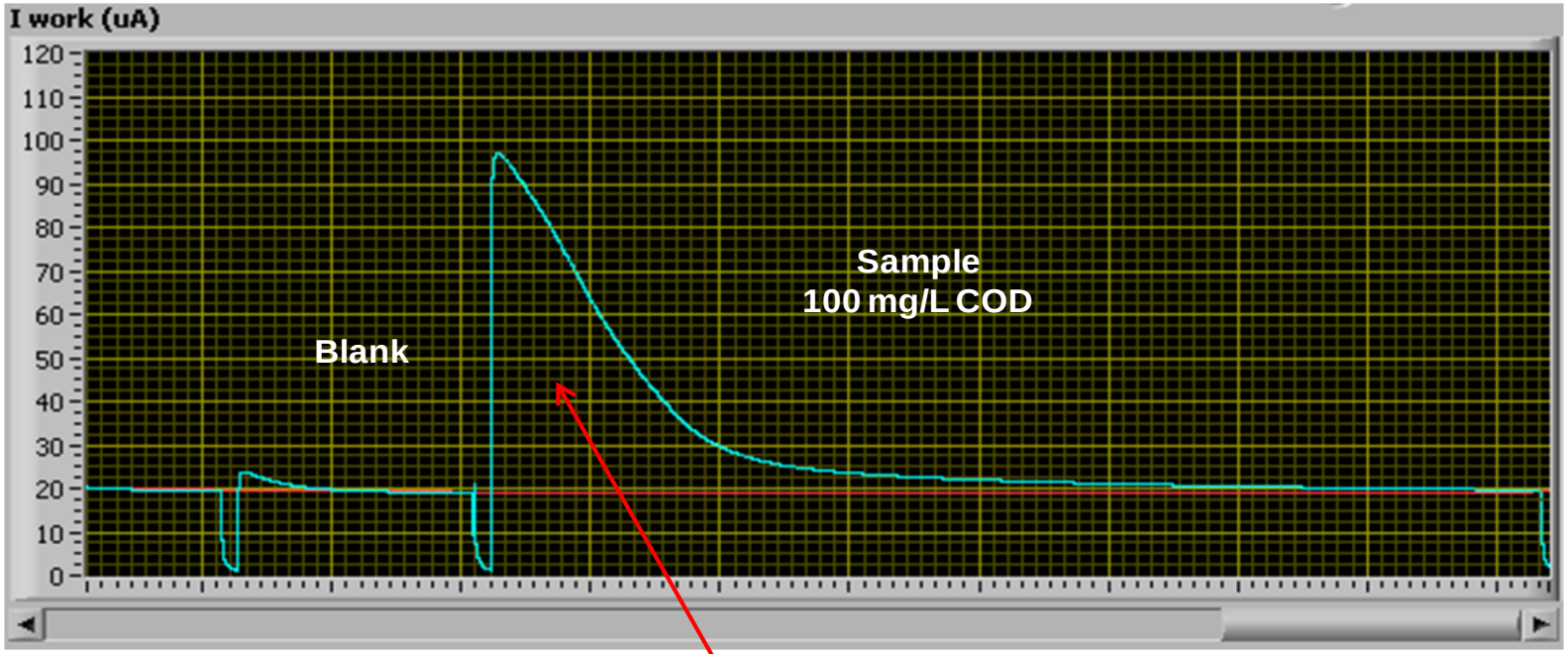


A Nanotechnology Based Approach



- Roughly 2 times the oxidizing power vs. dichromate
  - i.e. Benzene, 1.8 by COD_{Cr} and 2.6 by PeCOD®

Electrons to COD



Time 5 min

Area under curve = Q_{net}

COD = $k \cdot (Q_{net} - Q_{blank})$

Chilean Mill's Findings Using the peCOD Method

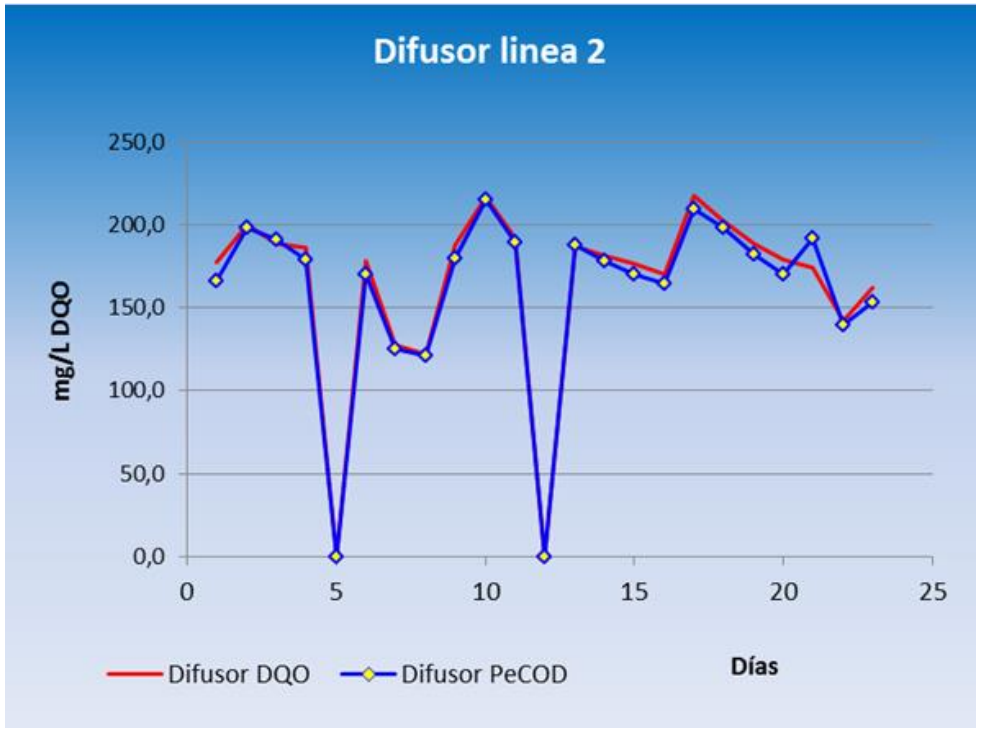


Figure 1: peCOD (blue) versus traditional method (red) for COD analysis at Diffusor Line 2.

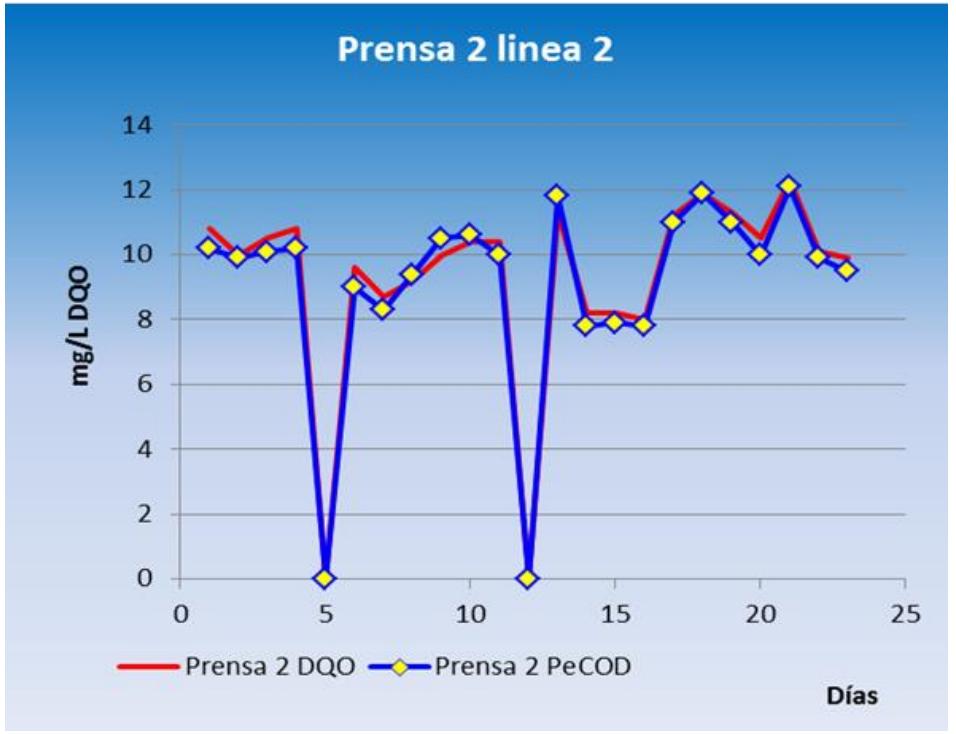
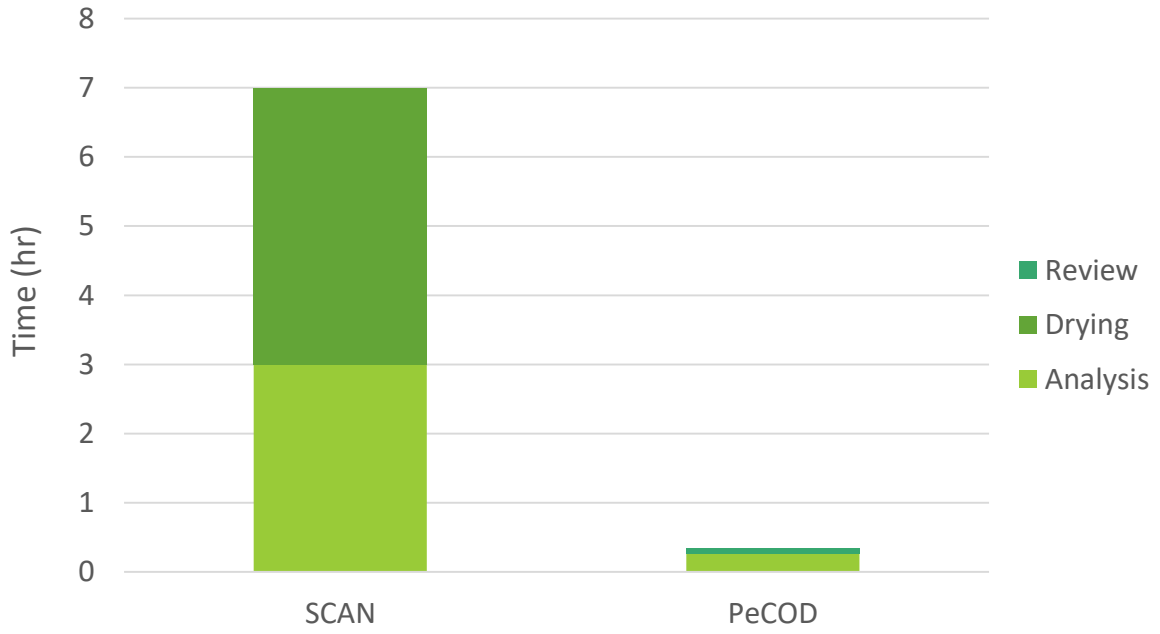


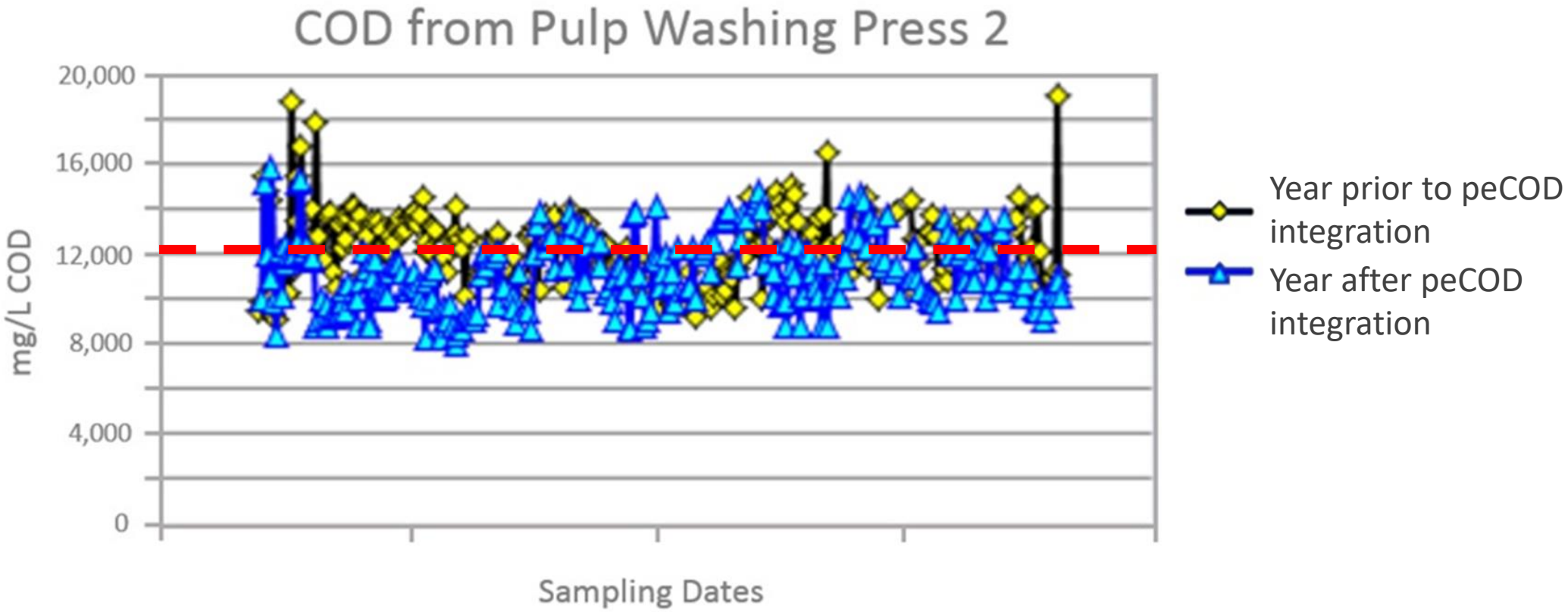
Figure 2: peCOD (blue) versus traditional method (red) for COD analysis at Press 2, Line 2.

Findings Using the peCOD Method Cont'd

- Decreased time in analysis:
  - SCAN method
    - 3 hours for COD analysis + 4 hours for drying
    - Total Time: 7 hours
  - peCOD method
    - 0.27 hours (16 min.) for COD analysis + 0.08 hours (5 min.) for review
    - Total time: 0.35 hours (20 min.)



Findings Using the peCOD Method Cont'd



- The graph shows a decrease in COD events for blue (peCOD integrated) compared to yellow (pre-peCOD integration)

Economic Evaluation

Annual reagents cost for COD analysis							
Methods	Total Analyses			Boxes Monthly	Cost (USD)	Cost Monthly (USD)	Cost Annually (USD)
	Daily	Monthly	Annually				
SCAN Method	12	360	4320	15 (25 vials per box)	30.00	450.00	5,400.00
	Total Analyses			Reagent Use Monthly [L]	Cost Reagents (USD/1L)	Cost Monthly (USD)	Cost Annually (USD)
	Daily	Monthly	Annually				
PeCOD Method	12	360	4320	2.5	60.00	150.00	1,800.00

- Switching from the SCAN method to peCOD method resulted in savings in reagents costs by 66.4%
- Saving 3,600 USD/year

Economic Evaluation Cont'd

Excess ClO_2 per event						
	Line 2			Line 1		
COD [kg /ton]	ClO_2 consumption [kg/ton]	ClO_2 consumtion [kg/day]	ΔClO_2 [kg/day]	ClO_2 Consumption [kg/t]	ClO_2 consumption [kg/day]	ΔClO_2 [kg/day]
10-12	16.3	23,651.3	3,337.3	16.5	12,969	1,807.8
13-19	18.6	26,988.6		18.8	14,776.8	
	Production (ton/d)		1,451	**Production (ton/d)**		786

- 13-19 kg/ton of COD represents a COD "event"
- An increase in 3kg COD/ton = increase in 1kg of ClO_2 consumption in the bleaching process
- Chemicals saving of approximately 2,237kg of ClO_2 per day, considering an event in both lines

Risk Assessment of COD Test Method

- SCAN Method:
  - Heat
  - Hazardous chemicals
  - Hazardous waste disposal
  - Significant

- peCOD Method:
  - No heat
  - Reagents are safe
  - Waste is safe (can go down the drain)
  - Tolerable

Conclusions

- Safety:
  - Decreased risk from significant to tolerable
  - Improved health and safety for workers

- Environment:
  - Reduced contamination to the effluent (eliminated excess ClO_2 use)
  - Eliminated hazardous waste, generated using the traditional COD method

- Savings:
  - COD analysis time reduced by 95%
  - Consumption of chemical reagents for COD analysis decreased by 66.4%
  - Management of ClO_2 consumption in the bleaching process resulted in bleaching chemical savings, over 2000kg of ClO_2 when an event was avoided each day

Conclusions

- Operators have peCOD results in less than 20 minutes
- PeCOD generated chemical savings, which means money savings!
- Improved Health & Safety, and Profitability
- Mill receives national award for improving sustainability
- 5 PeCOD units now in 2 mills

Thank You!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Questions?

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