Improved Mill Performance and Wastewater Treatment with new COD Monitoring Technology
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COD - Chemical Oxygen Demand

• COD is the amount of oxygen required to fully oxidize organic matter
  – Used as a measurement of the oxygen-depletion capacity of a sample contaminated with organic waste

• COD is significant to the bleaching process
  – Impacts the required chemical dosage used for pulp bleaching

• High COD = greater consumption of chemicals
  – Excess bleaching chemicals added to the process to compensate
At mills the impact of dissolved organics can have a large influence
  – Cost and performance especially when targeting aggressive discharge targets

Reasons for reducing water usage
  – Costs
  – Regulatory compliance
  – Environmental performance
  – Security of supply

Here to present summary of recent international work on novel rapid COD method and use with new water treatment technologies and methods at various stages of the pulp and paper wastewater treatment processes
Traditional Dichromate COD Method

- Hazardous chemicals used
- Concentrated Acid, Potassium Dichromate & Mercury
- Heat chemicals to 150°C
- 2-3 hour process
- Lab based only
  - COD$_{Cr}$
PeCOD® Method

- Results in less than **15 minutes**
  - final effluent in <7 minutes
- A patented technology that measures COD by oxidising organic matter by **photoelectric method**
- PeCOD eliminates the use of **mercury and potassium dichromate**
- **Safe** for both the environment and the analyst
- **Accurate** method with a detection limit of 0.7 mg/L, and upper range of 15,000 mg/L
- Allows for direct feedback
  - “Turn the Dial” response
PeCOD® COD Analyser Components

• Consumable Items:
  – Calibrant Solution - COD Standard
  – Electrolyte (for dilution)
  – Nano Sensor
A Nanotechnology Based Approach

To external circuit and auxiliary electrode

Roughly 2 times the oxidizing power vs. dichromate

\[ i.e. \text{ Benzene: } 1.8 \text{ by } \text{COD}_{\text{Cr}} \text{ and } 2.6 \text{ by PeCOD}^{\text{®}} \]
Electrons to COD

Area under curve = $Q_{net}$

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

Time 4 min
PeCOD Configurations

Benchtop L100

Automated L100

Online L100

Online P100
Case Study

- Chilean Mill
- Global company that produces many types of wood products
- Previously using SCAN-C 45:00 COD method
- Total 7hr test time meant deficiencies and improper dosing
- PeCOD allows operators to respond to events
Chilean Mill’s Findings

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.

Validated the PeCOD with respect to the standard SCAN method
Chilean Mill’s Findings

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

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

• Environment:
  – Reduced contamination to the effluent
  – 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%
  – Also results in lower organics in waste water plant and further reductions in chemical and energy used
  – Total savings over 12 months were $3 million dollars

National award for improving Sustainability, Health & Safety, and Profit

They now have 5 PeCOD units in 2 mills

Engineers can ALWAYS have a result within 15 min, sampling from any point
Industrial & Municipal

• Feb. 2016 Ontario approved peCOD method for use with domestic and surface waters
  – Replaces the standard dichromate methods E3170 and E3246 in Ontario

• Actual cost per sample compared to dichromate
  – Can be 50% less
  – Includes hazardous waste disposal for dichromate

• Major benefits in faster, more frequent sampling:
  – Real time incoming load monitoring
  – Quick and simple investigations for discharge

• Wide range of case studies
  – Municipal, Brewing, Wastewater treatment, Aluminium Manufacturing, etc.
CORECOD Project

- Novel concepts for Recalcitrant COD reduction in Pulp and Paper industry
- PeCOD chosen as the COD testing solution as rapid test results with true COD method required
  - Not selected COD$_{Cr}$, TOC, UV254
- A comparison of methods for many different effluents from kraft and mechanical pulp mills.
Key Experimental Findings

- peCOD method is applicable to Pulp & Paper wastewater
- peCOD method is the first method in 60 years to be an alternative, true oxidation method for COD
- H₂O₂ is NOT an interference for the peCOD method
  - H₂O₂ is a positive interference for the COD₇ Cr method
  - Critical finding for bleaching and advanced oxidation processes in general
  - Can be used to optimise bleaching process and provide correct, trusted results in the influent
CORECOD Project Outcome Utilisation

Influent → 1ry & 2ry Treatment → 3ry AOP Treatment

- Hard COD Reduction by AOP – 300ppm to 50ppm
- peCOD applicable to all grab sample points of interest and checks UV254 (since it is a surrogate)
**COD<sub>Cr</sub>**

- Laboratory, PPE, 8hrs/day, 5 days/week
- Operators operating “blind” at other times

**PeCOD® Analyser**

- In plant, 24/7
- Operators do the analysis and get COD when they want and need it
- From paper machines, bleaching control, wastewater treatment optimization, nutrient control and effluent compliance
- Used in both laboratory and plant environments

Matrix Specific Alternate COD Method Approval by PeCOD Adoption in Multiple Countries Including Finland
Opportunity for Pulp & Paper Mills

- Begin with PeCOD in Laboratory Operations
- Improve health and safety for everyone
- Rapid COD results delivered to operational engineers
- Impactful decisions made from fast COD results increases profit