Veolia Technologies for Mine Water Treatment

CONFEDEM Meeting in Madrid
October 10, 2013

Manuel Gómez – Director Desarrollo de Negocio, Zona Centro

Veolia Water Solutions & Technologies
Veolia Water Solutions & Technologies
Global leader in water treatment

- 100% subsidiary of Veolia Water
- Specialized in water and wastewater treatment for industries and municipalities
  - Technological solutions
  - Design-Build
  - Associated services
- 10,805 employees, over 60% researchers, engineers, project managers
- Over 350 proprietary technologies
- A customer-focused organization
  - Corporate Technical Research & Innovation
  - Technology Centers
  - Aquafab Standard Product Platform
  - Hydrex Platform - Specialized Water Treatment Products - Green chemistry
- Sustainability concerns
  - Water & Carbon footprint assessment for water management
  - Water Impact Index
Veolia Water Solutions & Technologies Iberica

- Offices: Madrid, Barcelona, Guipúzcoa, Tenerife, Zaragoza

- Headcount: **280 employees**

- Activities: **Design & Build, solutions and operations**

- Municipal and Industrial market, water & wastewater treatment
Creating Water Solutions for Mining

1. PRE-TREATMENT
   - Groundwater, surface water, greywater
   - Sewerage disinfection
   - Pipeline supply
   - Process water treatment
     - Screening
     - Flotation
     - Clarification
     - Reverse Osmosis
     - Membrane technology
     - Deionisation
     - Translation from the upstream and process water
   - Raw Water Source treatment (SWST)
   - Thermal Disinfection (TND)
   - Pipeline supply and conveyance

2. LEACH LIQUOR FILTRATION
   - Recovery of precious metals from leach stream
     - Process filtration
     - Vacuum decompression
     - Pressure filtration
     - Centrifugation

3. PROCESS WASTEWATER TREATMENT
   - Removal of contaminants including solids, heavy metals, cyanides, arsenic, selenium, iron, manganese, chromium, etc.
     - Neutralisation
     - Clarification
     - Filtration/De-salination
     - Solids polishing
     - Cyanide oxidation
     - Chemical metal precipitation/generation destruction
     - Sludge de-watering and drying
     - Inertisation and crystallisation

4. TAILINGS POND
   - Downstream and drying
   - Water Recovery and Reuse
   - Discharge compliance
   - Process water balance control
     - Clarification
     - Filtration
     - Cyanide oxidation
     - Filtration/de-salination
     - Ultra-filtration
     - Neutralisation
     - Softening

5. ACID/ALKALINE MINE DRAINAGE
   - Mine water control
   - Process water balance control
   - Groundwater reclamation
     - Clarification
     - Low pH Membrane processes
     - Mixed liquor and reverse osmosis
     - Enhanced biological processes (MBBR, AAO)
     - Metals precipitation - High Density Sludge
     - Chemical precipitation - Granular media filtration
     - Zero Liquid Discharge
     - Sea-water and crystallisation
     - High Recovery Reverse Osmosis
     - De-ionisation/Desalination

6. SOLUTIONS MINING and/or RESOURCE RECOVERY
   - Product recovery and water reuse
     - Desorption and crystallisation
     - Mineral precipitation
     - Ice exchange
     - Advanced membrane technologies
     - Liquid liquid extraction
     - Sludge de-watering and drying

7. SERVICES
   - Total validated system lifecycle compliance
     - Service contracts
     - Supply and support infrastructure
     - Chemical supply and logistics of distribution
     - Local support staff
     - Spare parts and consumables
     - Replacement parts
     - Water analysis service
   - Equipment leasing
   - Service Choice on site
     - Expansion and modernisation of treatment plants
     - Lifesaving
     - All site and long-term solutions
     - Water treatment chemistries
     - Complete water cycle management & outsourcing

VEOLIA WATER
Solutions & Technologies
Wide range of solutions

Technologies

- Enhanced clarification & softening for higher TSS water: **Multiflo™**
- High speed clarification & softening: **Actiflo™**
- Heavy metals removal: **MetClean™**
- Micro screen filtration: **Hydrotech™**
- Wide range of standard **filtration solutions**
- Membrane **filtration** (micro, ultra & nano-filtration, reverse osmosis)
- Ion exchange
- Moving bed biological reactor: **AnoxKaldnes™**
- Evaporation and crystallization: **Evaled™ - HPD**
- **Sludge** treatments

Services

- Chemicals for water treatment: **Hydrex™**
- **TechnoServices**: spare parts and consumables, technical assistance and specialized advice
- Temporary mobile water solutions: **Aquamove™**
- Operation plant and **outsourcing**
- Financing capacity in some projects
HPD Evaporation and Crystallization

- Evaporation solutions for all types of markets and industries:
  - Salt & caustic soda treatment, black liquor concentration, brine...
  - Potash and soda ash brine recovery

- Crystallization solutions for all types of markets and industries:
  - Solutions for marketable table salt and brine plants (NaCl, Na2SO4, KCl, ...)
  - ZLD solutions

- Advantages for salt plant: water and salt recovery

- Advantages for ZLD plants: highest water recovery and final solid product that can be manage with minimum environmental impact
Case Study: Fertilizer / Resource Recovery

Iperpotash, SA (ICL)

Suria, Barcelona, Spain

- Recovery from Potash Production
  - 750,000 tons/yr of chemical/food-grade sodium chloride
  - Up to 50,000 tons/yr of premium white potash

- Process System Overview
  - (2) Single-stage HPD® salt crystallizers
  - (1) Multi-stage HPD-DTB potash crystallizer system
  - ACTIFLO® high-rate clarification system

- Closed loop system
  - Captures leachate
  - Re-use of produced condensate

- Design-Build Project
Strong local presence for key players in the Mining Industry
Veolia Technologies for Mine Water Treatment

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Robert L. Zick – Director, Mining Market
Veolia Water Solutions & Technologies
Contents

1. Dense Sludge Technology
2. Zero Liquid Waste Technology
3. Sulphate Reduction Technology
4. Molycorp – Rare Earth Mine
Veolia’s DenseSludge Technology

- Technology Development
- Process Descriptions and Benefits
- Selected Project Experience
DenseSludge

- The original process (HDS) was developed at Bethlehem Steel over 30 years ago.
- It was developed to reduce sludge volumes in metal bearing wastewaters including Acid Mine and Acid Rock Drainage (AMD and ARD).
- First mining application – Consolidation Coal Company’s North Branch Mine in West Virginia in 1994
DenseSludge – Physical Descriptions

What is the DenseSludge process?

- Removal of Water Molecules from Sludge
- Sludge from Conventional Precipitation Process is Amorphous in Character
- Viscosity and Density of Sludge Increases
- Distinct Patterns of Crystals Appear
- Water of hydration is removed from the molecules
Scanning Electron Micrographs (SEMs) of Conventional and DenseSludge Samples

Sulfuric Acid Pickling of Steel Pipe

Conventional Sludge

DenseSludge
Simplified Schematic of Single Stage Process

(Single Stage Neutralization)

Alkali Source

Sludge Conditioning Tank

Untreated Wastewater

Neutralization Tank

Sludge Underflow (Continuous)

Clarifier

Treated Effluent

Sludge to Mine Disposal (Intermittent)
Principles of the DenseSludge process:

- Recycle sludge from the clarifier underflow
  - Typically between 5:1 and 20:1 recycle ratio is used (sludge solids : precipitating solids)
  - Clarifier underflow sludge pumps have VFDs to change the recycle ratio
- Mix recycled sludge with the alkali (lime or caustic soda)
- Use this “Alkalized” sludge as the neutralizing agent.
- As sludge is recycled, particles grow; metals grow in layers like an onion and gypsum crystals increase in size.
- Control pH in precipitation reactor
- Remove or “blowdown” a portion of the sludge intermittently to maintain the desired density of underflow slurry
DenseSludge Results and Benefits

The major benefits for DenseSludge versus Conventional:

1. >20% solids by weight in clarifier underflow
2. More efficient use of neutralizing agent (lime)
3. Decreases sludge blanket in clarifiers
4. Reduction of torque on clarifier drive
5. Reduction in footprint of clarifier (an increased rise-rate through the clarifier is achieved using the DenseSludge process compared to a conventional precipitation process)
6. Reduced scaling from gypsum (calcium sulphate) formation
## DenseSludge Mine Drainage Treatment Selected Projects

- **Minera Chinalco Peru** – Kingsmill Tunnel Discharge near Concentradora Mahr Tunnel in Department of Junin, Peru (Morococha Mining Region)
- **Atlantic Richfield Company** – Horseshoe Bend Seep in Butte, Montana at Berkeley Pit Site
- **Morgantown Energy Producing Co. (MEPCO)** – Steele Shaft Site near Garards Fort, Pennsylvania (PA)
- **PA Bureau of Abandoned Mine Reclamation** – Treatment of minepools for Lancashire Mine #15 and Hollywood Sites near Ebensburg, PA and near Hollywood, PA
- **CONSOL Energy** – Treatment of minepools at Flaggy Meadows, North Branch, and Blacksville #2 Mine Sites near Morgantown, Bayard, and Wana, West Virginia, respectively
- **LTV Steel Company** – Treatment of minepool for Clyde Mine near Clarksville, PA
Selected DenseSludge Project #1 – General Information
Kingsmill Tunnel AMD Project, Morococha Mining Region, Peru
Integrated with Chinalco’s Toromocho Copper Mine Project

- Design/Construct Project Team – Veolia and Cosapi S.A., a Lima, Peru-based Engineering and Construction Company
- Minera Chinalco Peru – Consultants: AMEC, design oversight and Grana y Montero, construction oversight
- Final Owner/Operator – Minera Chinalco Peru (the Chinese Aluminum Company)
- Design Flow Rate - Peak is 5,040 m³/hr, Average is 3,960 m³/hr
- Project Start-Up – 2010
- Constructed Cost – $35 Million US
Kingsmill Tunnel DenseSludge AMD Treatment Facility – Moracocha Mining Region in Peru
Selected HDS Project #2 – General Information

Atlantic Richfield Company (Formerly Anaconda Copper)
Horseshoe Bend WTP in Butte, Montana

- Contract Basis for Veolia – Two phases of Design Services, Major Equipment Procurement, Construction Management, and Start-Up/Training
- Design Team – Veolia and Butte, MT Engineering Firms: MSE Technology Applications, and HKM Engineering
- WTP Operator – Montana Resources (a US copper producer)
- Design Flow Rate – 1,100 m³/hr
- Two-stage precipitation and clarification process
- Installed Cost – $23 Million US
HSB Water Treatment Facility Process Flow Diagram

- HSB Water
  - Equalization Basin
  - Influent Pump Station
  - Discharge to Silver Bow Creek
  - Sludge Blow-Down to Berkeley Pit

- Air
  - 1st Stage PH Adjust
  - 1st Stage Clarifier
  - Alk. Tank
  - 2nd Stage PH Adjust
  - 2nd Stage Clarifier
  - Alk. Tank
  - Effluent Pump Station

- Lime System
  - Polymer System

- Effluent Lagoon
Atlantic Richfield’s Horseshoe Bend Dense Sludge AMD Treatment Facility – Butte, Montana
2 Zero Liquid Waste

A regulatory driven approach to mine water treatment
The Zero Liquid Waste (ZLW) Concept

- Many mine sites are required to remove sulphates and/or chlorides from mine water before discharging to a river or stream.

- Conventional treatment for pH, metals, and total suspended solids removal (TSS) before discharge to receiving streams does not remove sulphates or chlorides (salts) to levels required to meet new discharge standards.

- The Zero Liquid Waste concept was developed to meet new requirements for salt removal in addition to removal of metals and TSS.
ZLW and ZLD Process Similarities

**ZLW**
- **Feed**
- **PRE-TREATMENT** → **MEMBRANE TREATMENT** → **SLUDGE DEWATERERING** → **EVAPORATOR & CRYSTALLIZER** → **Clean Water Discharge**
  - Distillate
  - Crystals
- **Salt cake to disposal or recovery**

**ZLD**
- **Feed**
- **PRE-TREATMENT** → **MEMBRANE TREATMENT** → **SLUDGE DEWATERERING** → **EVAPORATOR & CRYSTALLIZER** → **Process reused water**
  - RO permeate
  - Distillate
- **Process reused water**
  - Crystals
- **Salt cake to disposal or recovery**
CONSOL ENERGY
Mannington, West Virginia Water Treatment Facility, USA

Client description:
• One of America’s largest producers of natural gas and coal
• Products help to provide over 70% of the power supply in the US

Client Needs:
• 3500 gpm Zero Liquid Waste mine water treatment facility
• Commercial operation began by May 30, 2013

Veolia’s Solution:
• DB: $95M – Pittsburgh office contract award in April 2011
  Pittsburgh: Softening & RO Systems
• Chicago: HPD® Evaporator/Crystallizer
• O&M: $5 M/yr - Veolia Water O&M contract award in May 2011, 10-year term with a 5-year renewal option

Technical highlight:
• Lime Softening with Turbomix™ technology
• Solids setting with conventional clarifiers
• 85% recovery through RO
• Solid waste (softening sludge and salt crystals) for disposal in on-site landfill
Design Basis – CONSOL Mannington, WV Water Treatment Facility

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>MINE WATER</th>
<th>LEACHATE (PROJECTED)</th>
<th>REQUIRED EFFLUENT*</th>
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<tbody>
<tr>
<td></td>
<td>MAX</td>
<td>AVG</td>
<td></td>
</tr>
<tr>
<td>Design Flow, GPM</td>
<td>3500</td>
<td></td>
<td>5 (7,200 gpd)</td>
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<td>pH, S.U.</td>
<td>5 – 10</td>
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<tr>
<td>Calcium, mg/l</td>
<td>300</td>
<td>268</td>
<td>39</td>
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<tr>
<td>Sodium, mg/l</td>
<td>3,000</td>
<td>2,855</td>
<td>106,724</td>
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<tr>
<td>Magnesium, mg/l</td>
<td>200</td>
<td>144</td>
<td>0.02</td>
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<tr>
<td>Potassium, mg/l</td>
<td>10</td>
<td>12</td>
<td>958</td>
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<tr>
<td>Alkalinity, mg/l as CaCO3</td>
<td>700 - 1,200</td>
<td>1,045</td>
<td>0</td>
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<td>Chlorides, mg/l</td>
<td>1,500</td>
<td>1,356</td>
<td>148,219</td>
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<tr>
<td>Sulfates, mg/l</td>
<td>5,000</td>
<td>4,962</td>
<td>23,466</td>
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<td>Iron, mg/l</td>
<td>150</td>
<td>114</td>
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<tr>
<td>Manganese, mg/l</td>
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<td>1.7</td>
<td>0.01</td>
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<tr>
<td>Aluminum, mg/l</td>
<td>8</td>
<td>4</td>
<td>5.6</td>
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<td>Barium, mg/l</td>
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<td>Strontium, mg/l</td>
<td>10</td>
<td>8</td>
<td>2</td>
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<td>TDS, mg/l</td>
<td>11,000</td>
<td>11,000</td>
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<tr>
<td>TSS, mg/l</td>
<td>150</td>
<td>104</td>
<td>100</td>
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</table>

*Additionally, effluent must comply with all applicable in-stream water quality criteria specified by the state of West Virginia.
The ZLW concept uses Veolia technologies

- Lime & Soda Ash Silos
- Multimedia Filters
- RO Trains
- HPD Evaporator
- HPD Crystallizer
- Raw Water Tank
- 1st Stage Clarifier
- Sludge and Salt Dewatering Building
- Softening Systems with MULTIFLO Turbomix
CONSOL Energy – Mannington, WV WT Facility
Site Overview Looking Northeast
CONSOL Energy – Mannington, WV WT Facility
View Looking South, Landfill Upper Right
CONSOL Energy – Mannington, WV WT Facility
View Facing West
CONSOL Energy – Mannington, WV WT Facility
View Facing Northwest
3

Sulphate Treatment

A regulatory driven approach to mine water treatment
Two - Stage Sulphate Treatment Technology

- Reduces sulphate to < 50 mg/L by Two-Stage Process:
  - 1\textsuperscript{st} Stage: CaSO\textsubscript{4} Desaturation
    - SO\textsubscript{4} is reduced to <1,500 mg/L
  - 2\textsuperscript{nd} Stage: Advanced Chemical Precipitation (Ettringite)
    - SO\textsubscript{4} is reduced to < 50 mg/L
- Treated effluent can be reused.
## Discharge Requirements – Typical Irrigation Standards

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>250</td>
</tr>
<tr>
<td>Cl</td>
<td>200</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2</td>
</tr>
<tr>
<td>Mo</td>
<td>0.01</td>
</tr>
<tr>
<td>Na</td>
<td>35%</td>
</tr>
<tr>
<td>Al</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>0.10</td>
</tr>
<tr>
<td>Cd</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2</td>
</tr>
<tr>
<td>Co</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>0.20</td>
</tr>
<tr>
<td>V</td>
<td>0.10</td>
</tr>
<tr>
<td>Zn</td>
<td>2.0</td>
</tr>
<tr>
<td>Ca</td>
<td>60</td>
</tr>
</tbody>
</table>

All concentrations are in mg/L.
Proposed Concept

POND WATER ➔ PRETREATMENT ➔ NANOFILTRATION ➔ NF PERMEATE

BACK TO POND (OPTION - I) ➔ DESATURATION OF CaSO₄

OPTION II ➔ ADVANCED PRECIPITATION PROCESS ➔ TREATED WATER SO₄ < 50 mg/l

CaSO₄ ➔ CaSO₄ SLUDGE
Pretreatment before Nanofiltration

- Pretreatment includes iron coagulation, multimedia filtration (MMF) and Green Sand filtration (if needed to reduce manganese)
- Veolia Multiflo Turbomix Technology for Pretreatment with MMF and Cartridge Filters
  - Mo reduced to < 0.05 mg/L
  - Fe reduced to < 0.3 mg/L
  - Mn reduced to < 0.05 mg/L
- Silt Density Index after MMF: 3 – 4
Nanofiltration Reject Treatment

- Precipitate $\text{SO}_4$ as $\text{CaSO}_4$
- Use lime or lime + $\text{CaCl}_2$ as sources of $\text{Ca}^{2+}$
- Recycle Ratio = mass of solids (CaSO$_4$) in the recycle line : mass of solids (CaSO$_4$) formed from the NF reject
- Goal is to reduce SO$_4$ to < 1,500 mg/L as SO$_4$ (theoretical solubility limit)
Basic Sulphate Precipitation Process

REJECT WITH HIGH SULPHATES (SO4 3200 and Calcium 1020 mg/l)

VEOLIA WATER (TURBOMIX) REACTOR

Ca^{2+} SEED

VEOLIA WATER SOLID /LIQUID SEPARATOR (MULTIFLO)

TREATED WATER SO4 < 1500 mg/l

SLUDGE RECYLE

CaSO4 SLUDGE FOR DISPOSAL
SULFATE TREATMENT SCHEMATIC
(Advanced Precipitation/Ettringite Process)

MEMBRANE REJECT → TURBOMIX WITH MULTIFLO

LIME OR CaCl2 → SEED

SO4 < 1800 mg/l → TURBOMIX PH: 11.5 – 11.8

LIME ALUMINUM

MULTIFLO

TREATED WATER SO4 < 100 mg/l

SLUDGE RECYCLE

SATURATED SOLUTION OF CaSO4

TO SLUDGE DEWATERING UNIT

ACID

AL(OH)3 REGENERATION TANK PH: 6.5

LIME SEED LIME OR CaCl2

SO4 < 1800 mg/l

SLUDGE RECYCLE

TREATED WATER SO4 < 100 mg/l

ACID

AL(OH)3 REGENERATION TANK PH: 6.5

LIME SEED LIME OR CaCl2

SO4 < 1800 mg/l

SLUDGE RECYCLE

TREATED WATER SO4 < 100 mg/l

ACID

AL(OH)3 REGENERATION TANK PH: 6.5
Conclusions

- NF with Proper Pretreatment is Capable of Reducing Sulphate to < target limit of 250 mg/L
- More than 98% Sulphate Rejection was Achieved
- **1st Stage Desaturation Process:**
  - Sulphate from NF Reject reduced to <1,500 mg/L in presence of a seed material with Optimum Sludge Recirculation Ratio.
- Seed material is added one time during the start-up of crystallization process
- Sulphate Removal is a combination of Chemical Precipitation and Adsorption Process.
Conclusions (contd.)

- CaSO$_4$ Crystal Growth Kinetics depends on the Water Quality, type and dosage of Seed Material, and sludge recirculation ratio

- 2nd Stage Advanced/Ettringite Precipitation Process
  - Sulphate reduced from 1,500 to <50 mg/L
  - > 90% aluminum regeneration is expected
  - Bench-scale continuous testing has demonstrated > 90% aluminum recovery
A regulatory driven approach to minewater treatment

Molycorp

Water treatment for rare earth minerals

Veolia Water

Solutions & Technologies
Molycorp Mountain Pass Mine – Project Executed by Veolia’s Dayton, OH & Pittsburgh, PA Offices

Client description:
- The only rare earth oxide (REO) producer in the Western hemisphere.
- Own and operate the world’s largest, most fully developed rare earth mine and oxide manufacturing facility outside of China.

Project description:
- Client Needs:
  - The mine site will be integrated with a power plant, a chlor-alkali plant, a processing mill, and a water treatment plant.
  - Treatment for waste streams recycle as feed streams to the chlor-alkali plant.
- Veolia’s Solution:
  - Contract value: 
    - DB: $39M + Equipment: $10M
  - BU synergy: 
    - Dayton: Sales lead & equipment provider
    - Pittsburgh: Process technology support & Turnkey Design Build of the water treatment plant
- Technical highlight:
  - Flow rate: 1000 GPM (227m3/h)
  - Technologies:
    - OPUS and Multiflo/Turbomix

Project Phoenix Fly-Over Video:
http://www.molycorp.com/Resources/PhotoTours/ProjectPhoenixFlyOver.aspx
Questions?
Thank You!