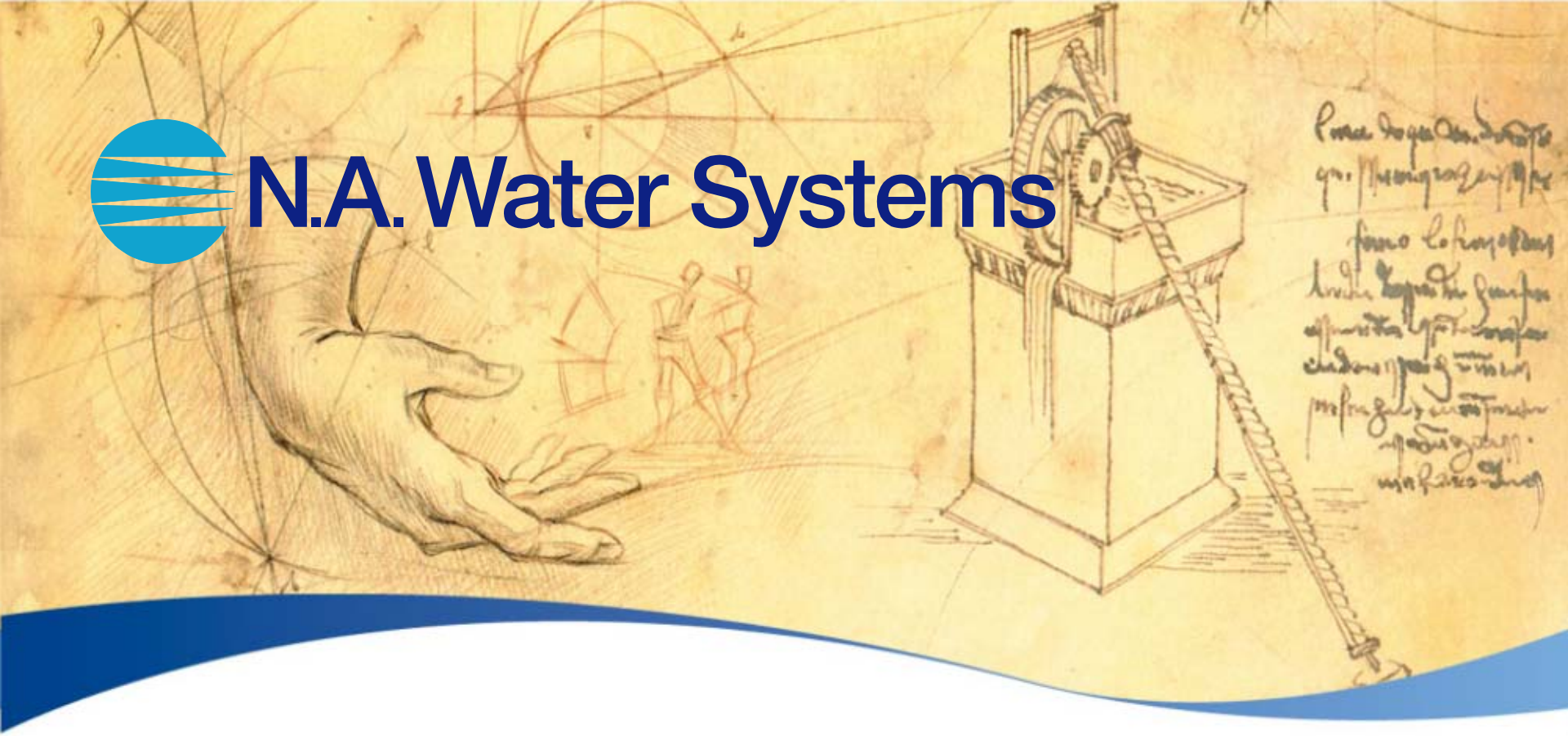

N.A. Water Systems

# Treatment of Acidic Industrial Wastewaters using LowpHRO™ Technology

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LNSP Nagghappan

VEOLIA WATER
Solutions & Technologies

# Acidic Wastewater

- Sources
  - Phosphate Manufacturing
  - Mining
  - Steel Mills
- Typical Acidic Wastewater
  - Hardness
  - Sulfates
  - Ammonia
  - Fluorides
  - Phosphates
  - Silica
  - Metals (Al, Fe, Mn, etc)
  - Total Dissolved Solids
- Disposal Options
  - Surface Water Discharge
  - Beneficial Re-use as Process Water/Plant Water
  - Off-site Disposal of Handling
  - Deep Well Injection

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# Treatment Options

- Single/Double Liming Process
  - High Chemical Costs
  - High Solids Generation
  - Issues Associated with Sludge Management
  - Inability to meet Effluent Quality – Conductivity, Ammonia, etc
- Reverse Osmosis Technology
  - High Quality Effluent
  - Scaling & Fouling Concerns
  - Moderate CAPEX & OPEX Costs
  - Effective & Reliable Technology
- Evaporation Technology
  - High Quality Distillate
  - Scaling & Corrosion Concerns
  - High Capital Costs – Exotic Materials
  - High OPEX Costs – Power

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# RO Technology Challenges

- Membrane Scaling Issues
  - Silica
  - Calcium Fluoride
  - Calcium Sulfate
  - Calcium Phosphate
  - Metals (Fe, Mn, Al, etc)
- Membrane Fouling Issues
  - Particulates
  - Biological
- Other Related Issues
  - Mechanical Pressure Limitation (Max: 1000 psig)
  - Membrane Salt Rejection Requirements (TDS, Total N, P, F, etc)
  - Membrane Life & Replacement Requirements
  - Reject Handling

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# Our Approach:

- Utilize Reverse Osmosis at a Low pH
  - Potential Advantages:
    - Rejection of Ammonia as Ammonium Ion
    - Scale control by promotion of soluble chemical equilibrium to prevent calcium sulfate, calcium fluoride and silica scaling
    - Rejection of Phosphates as $H_3PO_4^0$ and $H_2PO_4^-$
  - Overall Technology Goals:
    - High Quality Permeate
    - High Recovery Rate
    - Limited Sludge Generation
    - Use of Reject in Production

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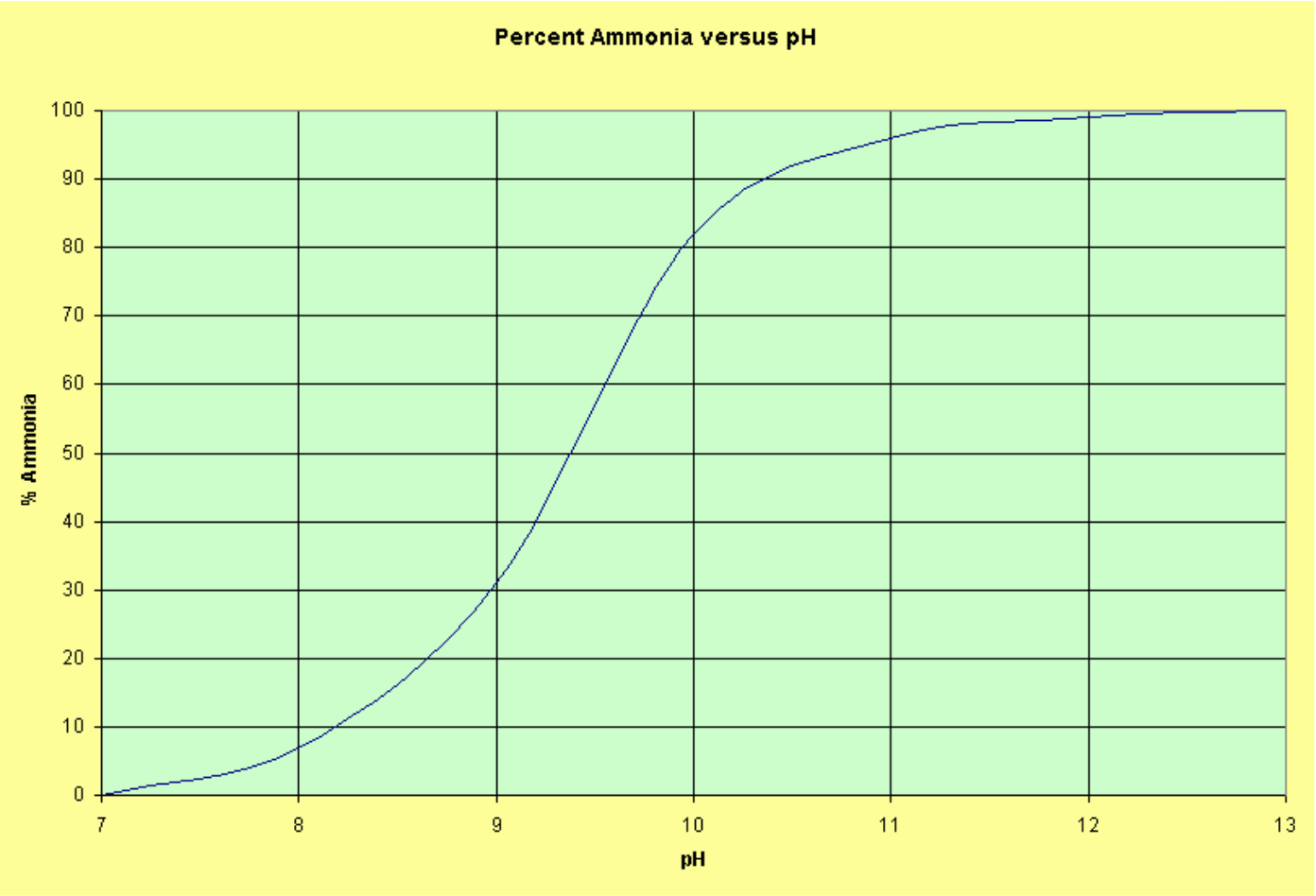
# Free Ammonia / Ammonium Ion Equilibrium

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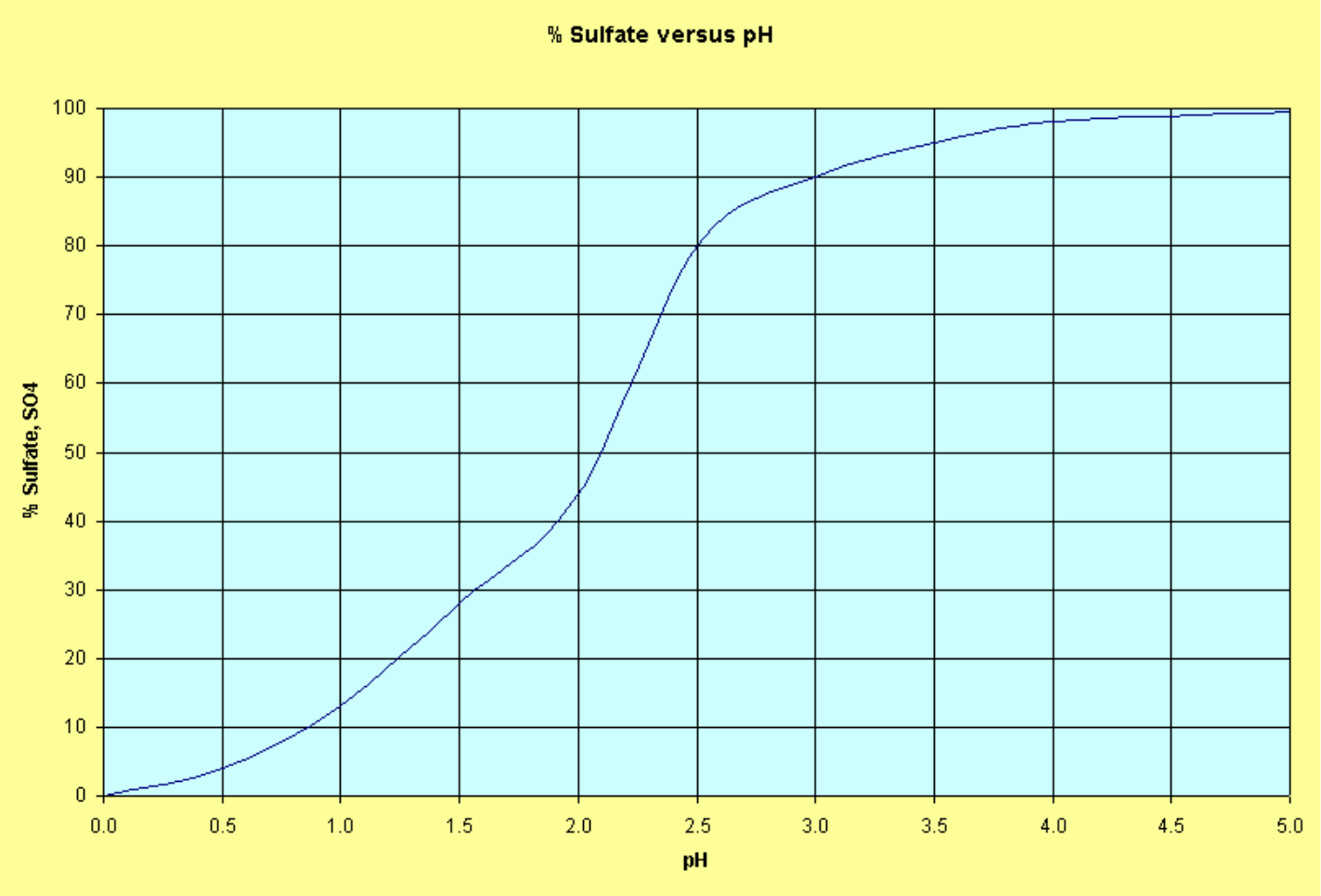
# Sulfate/Bisulfate Equilibrium

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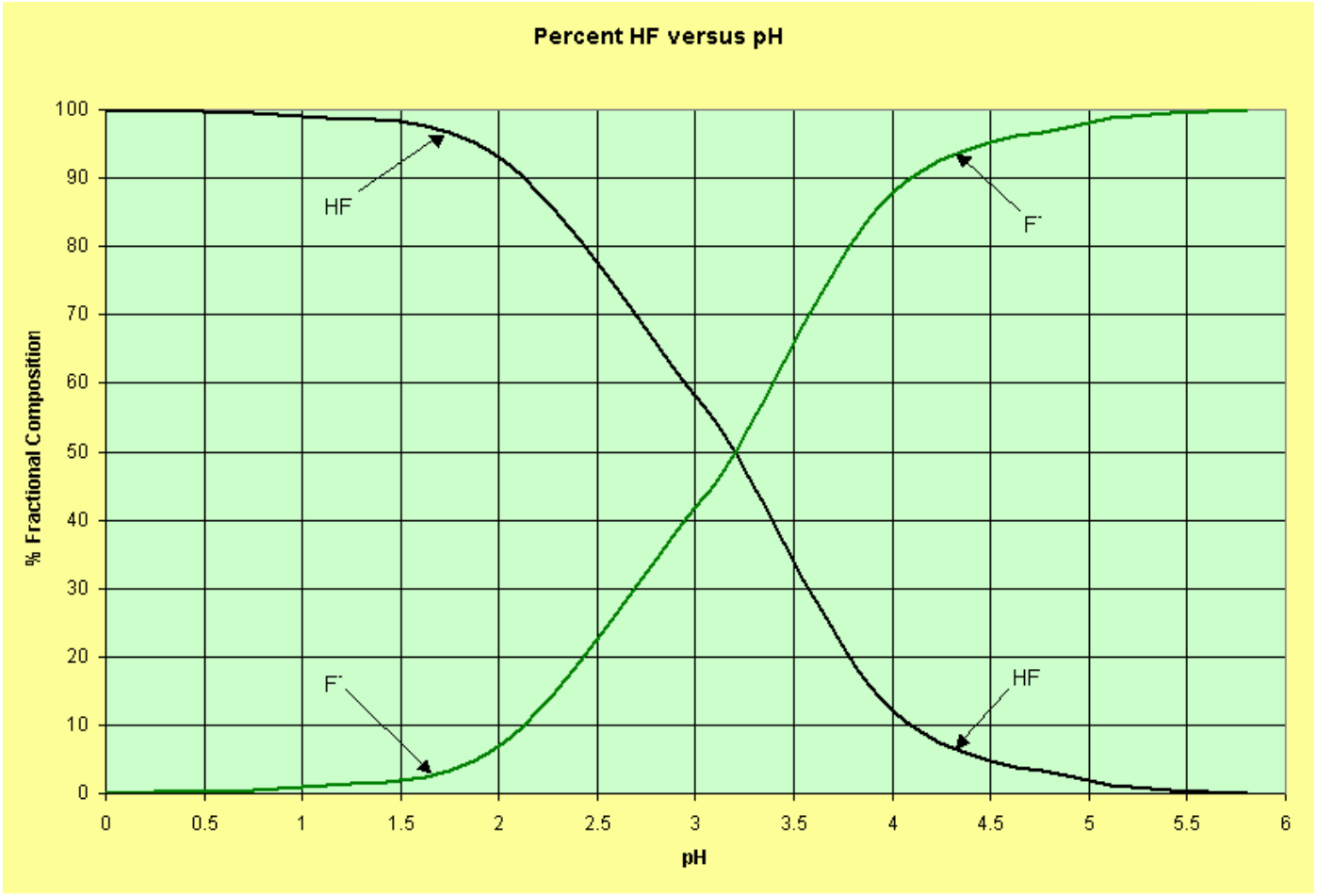
# Hydrofluoric Acid / Fluoride Equilibrium

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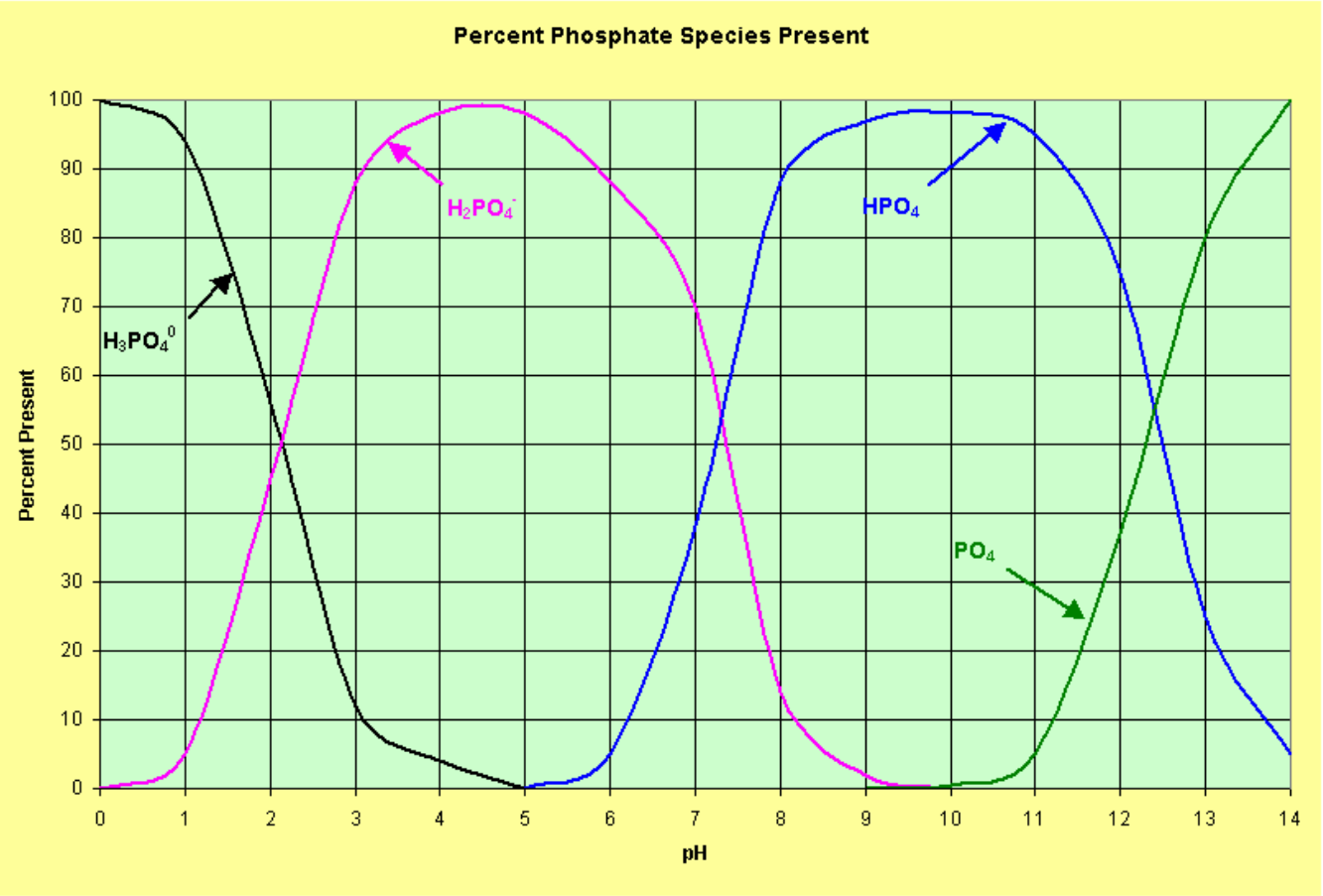
# Phosphoric Acid / Phosphate Equilibrium

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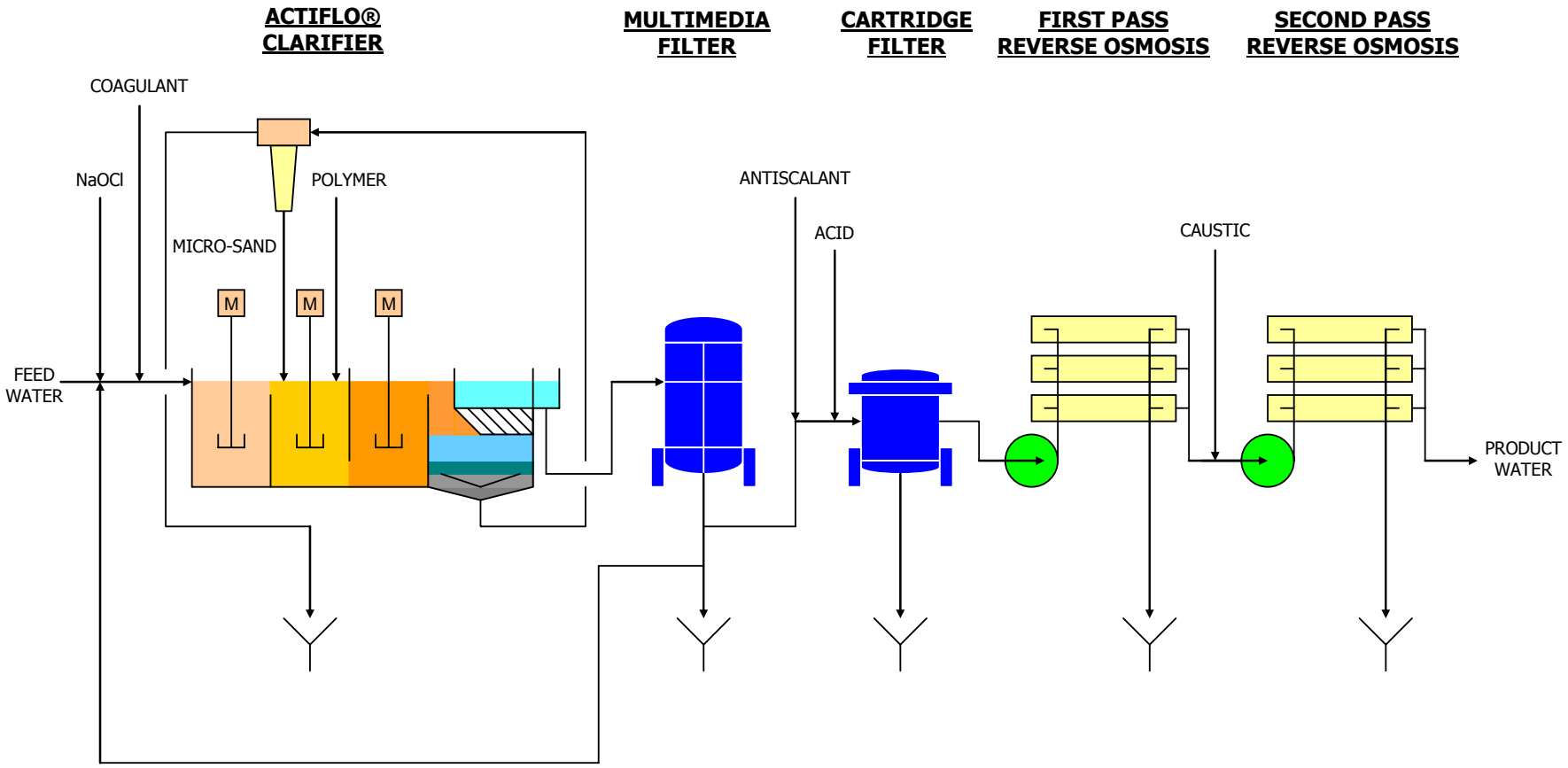
# LowpHRO™ Technology *PATENT PENDING PROCESS*

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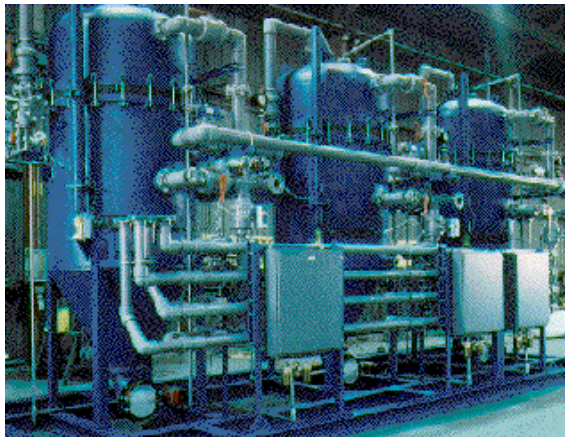
# LowpHRO™ Technology Discription

## > Technology Discription

- > Proprietary Low pH Coagulation Process
- > High Rate Pretreatment Process
  - Actiflo® Clarification
  - Multimedia & Cartridge Filtration
- > Effective Scaling Control
  - Proprietary Antiscalant Addition
  - Soluble Chemical Equilibrium Promotion
  - 1st Pass RO Operation @ pH < 3.5
  - Interstage Caustic Addition
  - 2nd Pass RO Operation @ pH > 6.0
- > Effective Fouling Control
  - Particulate Fouling
  - Bio-Fouling



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# LowpHRO™ Technology Discription

- Technology Discription (cont'd):
  - High Salt Rejection
    - Ammonia > 99%
    - Fluorides > 99.1%
    - Phosphates > 99.9%
    - Sulfates > 99.1%
  - Less CAPEX & OPEX Costs than Double Liming Process
    - 90 ~ 95% Less Alkali Demands
    - 90 ~ 95% Less Solids Generation

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# Case Study 1

- Project Location – Florida
- Source Water – Phosphate Pond Water
- Project Discharge Requirements
  - Surface Water Discharge
  - Conductivity < 1,275 µS
  - Ammonia < 30 mg/l
  - Phosphate < 15 mg/l
  - Fluoride < 10 mg/l
- Project Objectives
  - Low Chemical Demand
  - Low Solids Generation
  - High Salt Rejection
  - Low Life Cycle Cost

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# Case Study 1 - Influent Quality

| CATIONS | CONCENTRATION |
|---|---|
| CALCIUM, mg/l | 716 |
| MAGNESIUM, mg/l | 303 |
| SODIUM, mg/l | 1,360 |
| POTASSIUM, mg/l | 149 |
| ALUMINUM, mg/l | 112 |
| BARIUM, mg/l | 1.0 |
| STRONTIUM, mg/l | 21.0 |
| AMMONIUM, mg/l | 101.6 |

| ANIONS | CONCENTRATION |
|---|---|
| BICARBONATES, mg/l | - |
| CARBONATES, mg/l | - |
| HYDROXIDES, mg/l | - |
| SULFATES, mg/l | 4,523 |
| CHLORIDES, mg/l | 143 |
| PHOSPHATES, mg/l | 18,642 |
| NITRATES, mg/l | 5.0 |
| FLUORIDES, mg/l | 4,782 |

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# Case Study 1 - Influent Quality

| CONSTITUENT | CONCENTRATION |
|---|---|
| pH, standard units | 1.9 |
| TEMPERATURE, deg F | 77 |
| T. ALKALINITY, as $CaCO_3$ | - |
| T. Ammonia, as N | 130.7 |
| IRON, mg/l | **117.0** |
| MANGANESE, mg/l | **11.6** |
| SILICA, mg/l | **1,270** |
| BORON, mg/l | - |

| CONSTITUENT | CONCENTRATION |
|---|---|
| TDS, mg/l | 33,063 |
| Conductivity, µS | 24,800 |
| TSS, mg/l | **210** |
| TURBIDITY, NTU | - |
| TOC, mg/l | **132** |
| COD, mg/l | - |
| Total Sulfides, mg/l | - |
| Total Oil & Grease, mg/l | - |

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# Case Study 1 - Treatment Challenges

- Membrane Scaling Issues
  - Silica
  - Calcium Fluoride
  - Calcium Sulfate
  - Calcium Phosphate
  - Metals (Fe, Mn, Al, etc)
- Membrane Fouling Issues
  - Particulates (High TSS)
  - Organics (High TOC)
- Salt Rejection Requirements
  - TDS
  - Ammonia
  - Fluoride
  - Phosphate

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# Case Study 1 - LowpHRO™ Technology Performance

| Constituent | Feed Water | First Pass RO Permeate | Second Pass RO Permeate |
|---|---|---|---|
| TDS, mg/l | 33,063 | 562 | < 25 |
| Conductivity, µS | 24,800 | 1,850 | < 50 |
| Ammonia, mg/l | 102 | 5.3 | < 0.5 |
| Phosphates, mg/l | 18,641 | 208 | < 5.0 |
| Fluorides, mg/l | 4,782 | 185 | < 5.0 |
| Sulfates, mg/l | 4,523 | 70 | < 1.0 |
| Silica, mg/l | 1,270 | 13 | < 0.3 |
| Calcium, mg/l | 716 | 7.7 | < 0.2 |
| pH, standard units | 1.9 | 2.7 | 6.5 ~ 7.5 |

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# Case Study 2

- Project Location – South Africa
- Source Water – Coal Mine Water
- Project Discharge Requirements
  - Potable Water Reuse
  - Total Dissolved Solids < 450 mg/l
  - Calcium < 80 mg/l
  - Magnesium < 30 mg/l
  - Sodium < 100 mg/l
  - Chloride < 100 mg/l
  - Sulfate < 200 mg/l
- Project Objectives
  - Low Chemical Demand
  - Low Solids Generation
  - High Salt Rejection
  - Low Life Cycle Cost

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# Case Study 2 – Influent Quality

| CATIONS | CONCENTRATION |
|---|---|
| CALCIUM, mg/l | 550 |
| MAGNESIUM, mg/l | 192 |
| SODIUM, mg/l | 108 |
| POTASSIUM, mg/l | 11 |
| ALUMINUM, mg/l | 33 |
| BARIUM, mg/l | - |
| STRONTIUM, mg/l | - |
| AMMONIUM, mg/l | 5 |

| ANIONS | CONCENTRATION |
|---|---|
| BICARBONATES, mg/l | - |
| CARBONATES, mg/l | - |
| HYDROXIDES, mg/l | - |
| SULFATES, mg/l | 2,896 |
| CHLORIDES, mg/l | 35 |
| PHOSPHATES, mg/l | - |
| NITRATES, mg/l | 10 |
| FLUORIDES, mg/l | 1 |

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# Case Study 2 – Influent Quality

| CONSTITUENT | CONCENTRATION |
|---|---|
| pH, standard units | 2.7 |
| TEMPERATURE, deg F | 71 |
| T. ALKALINITY, as $CaCO_3$ | - |
| T. Ammonia, as N | 6.0 |
| IRON, mg/l | **175** |
| MANGANESE, mg/l | **29** |
| SILICA, mg/l | **25** |
| BORON, mg/l | - |

| CONSTITUENT | CONCENTRATION |
|---|---|
| TDS, mg/l | 4,072 |
| Conductivity, µS | 6,000 |
| TSS, mg/l | **475** |
| TURBIDITY, NTU | - |
| TOC, mg/l | 4 |
| COD, mg/l | - |
| Total Sulfides, mg/l | - |
| Total Oil & Grease, mg/l | - |

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# Case Study 2 - Treatment Challenges

- Membrane Scaling Issues
  - Calcium Sulfate
  - Aluminum Precipitates
  - Iron Precipitates
  - Manganese Precipitates
- Membrane Fouling Issues
  - Particulate (High TSS)
- Salt Rejection Requirements
  - TDS
  - Ammonia
  - Fluoride
  - Phosphate

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# Case Study 2.0 - LowpHRO™ Technology Performance

| Constituent | Feed Water | Single Pass RO Permeate |
|---|---|---|
| TDS, mg/l | 4,072 | < 90.0 |
| Calcium, mg/l | 550 | < 8.0 |
| Magnesium, mg/l | 192 | < 3.0 |
| Sodium, mg/l | 108 | < 5.0 |
| Chloride, mg/l | 35 | < 3.5 |
| Sulfate, mg/l | 2,896 | < 61 |
| Ammonia, mg/l | 5.0 | < 0.05 |

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# Merits of LowpHRO™ Technology

- High Salt Rejection
  - TDS > 98%
  - Ammonia > 99%
  - Fluorides > 99.1%
  - Phosphates > 99.9%
  - Sulfates > 99.1% %
- Less OPEX Costs than Double Liming Process
  - 90 ~ 95% Less Alkali Demand
  - 90 ~ 95% Less Sludge Generation
- Effective Pretreatment Process for Fouling Control
  - Proprietary LowpH Coagulation Process
  - Effective Removal of Particulates
- Effective Scaling Control
  - Promotion of Soluble Chemical Equilibrium
  - Proprietary Antiscalant Addition
- Reject Waste Re-use for Active Facilities

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