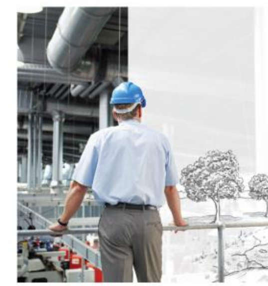
# Recovery of Clean Water and Metals from Mining Wastewater and solutions using Nanofiltration membranes



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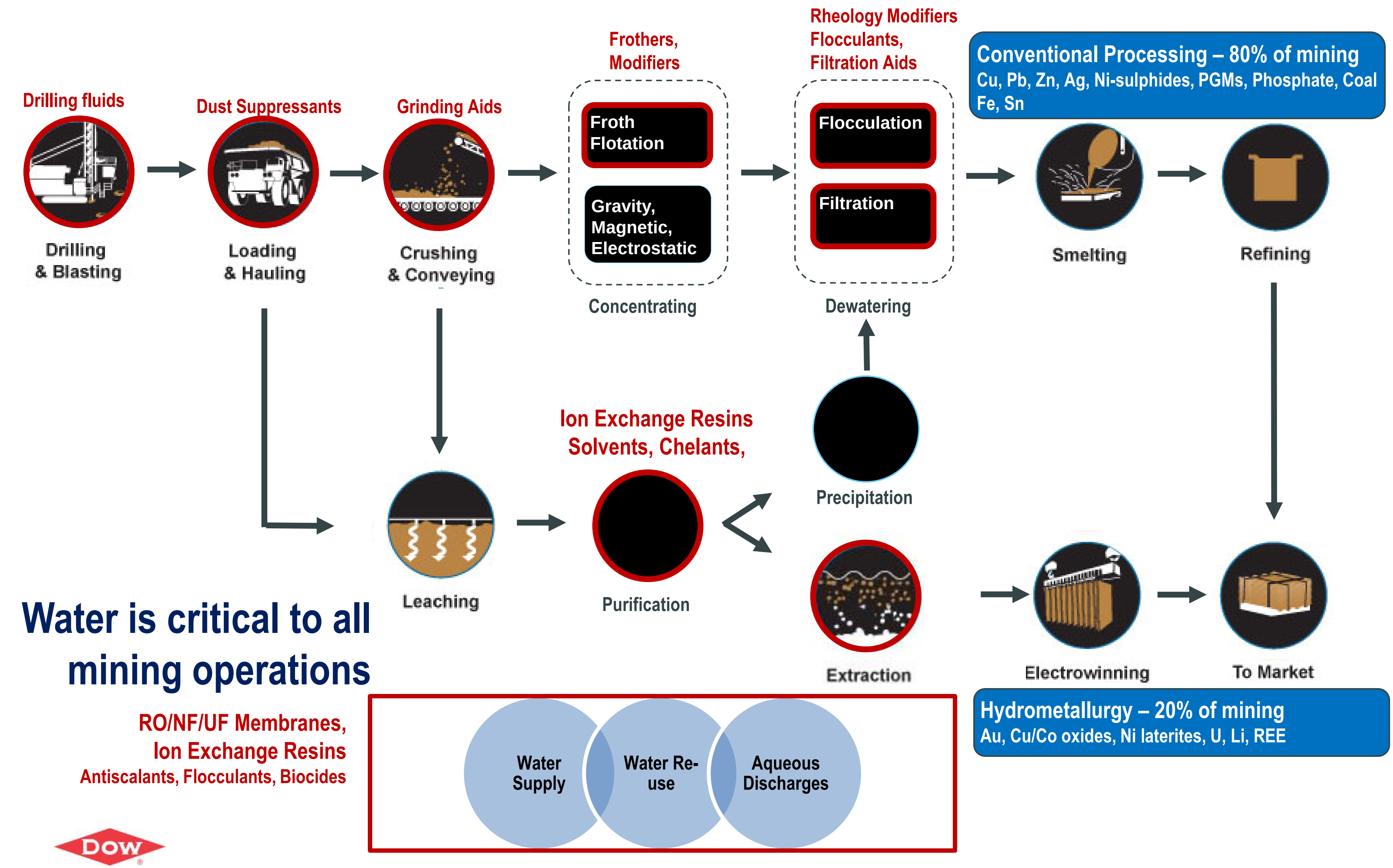
# Water is critical to all Mining operations




Source: Adapted from Freeport-McMoRan Copper & Gold Inc, SRI Consulting, Various Other Dow

# Dow Water & Process Solutions: At a Glance

*Our Strategy is to be the performance leader in applying differentiated technology and expertise to solve our customers' most challenging separation and purification problems.*

- Global Innovation Leader in Reverse Osmosis and Ion Exchange
- Our technologies process over 15 million gallons of water per minute globally

**$1B** REVENUE

**1900** EMPLOYEES

**8** MANUFACTURING PLANTS

**7** STATE OF THE ART **R&D CENTERS**

USA I SAUDI ARABIA I CHINA I SPAIN

ALIGNED WITH **4 MEGATRENDS**

**WATER I ENERGY I** HEALTH/WELLNESS **I** URBANIZATION

# Water & Separation Technologies

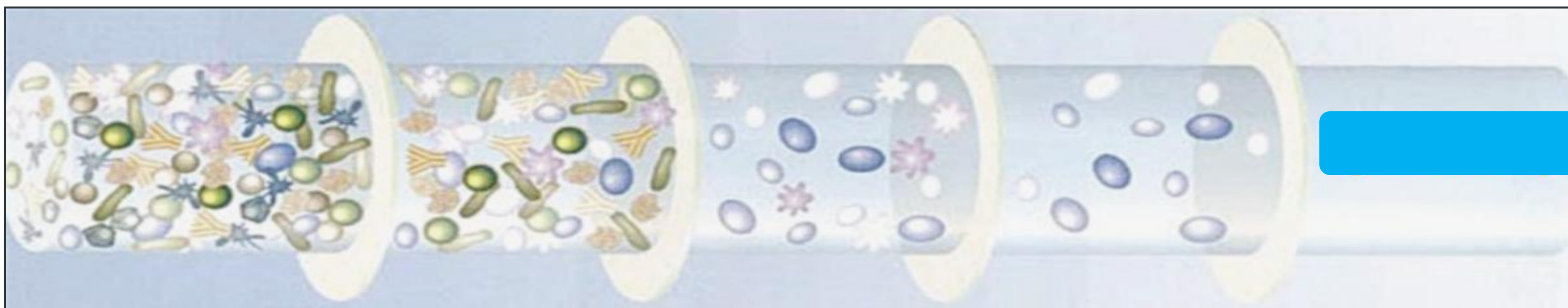
**Microfiltration**
Pore size: >0.05
PSI: 15 – 60

**Ultrafiltration**
Pore size: up to 0.05
PSI: 5 to 30

**Nanofiltration**
Pore size: .001
PSI: 90 – 150

**Reverse Osmosis**
Pore size:
PSI: 75 to 1000

**Ion Exchange Resins**
Pore size:
PSI: 50



**Filters High Molecular Weight Species**
Sand, silt, clays, giardia, algae, some bacteria, pre-treatment

**Filters Macromolecules**
All microbiological species, some viruses and humic materials

**Filters Small Molecules**
Virtually all bacteria, viruses, cysts, humic materials, removes alkalinity and $H_2O$ hardness

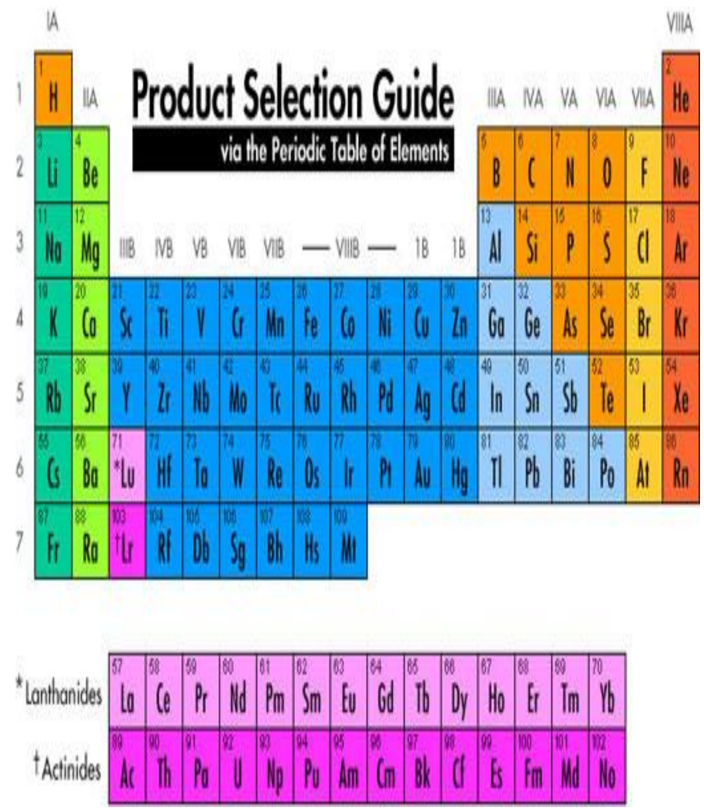
**Removes Salts, Ions, Color, LMW Species**
Nearly all inorganic contaminants, as well as radium, pesticides, cysts, bacteria and viruses

**Purifies and Changes**
Further removes metal ions and mineral content to soften the water or improve its purification. Changes water characteristics.

"Mechanical" Water Treatment Under Pressure → "Chemical" Treatment at Molecular Level

# Ion Exchange Resins Metal Recovery and Extraction

| Product | Functionality | Description |
|---|---|---|
| **AMBERLITE IRA743** | **N-Methyl Glucamine** | Boron removal |
| **DOWEX 21K XLT** | **SBA-Type 1** | 600µm uniform particle size, high capacity resin for uranium, gold ,zinc, and Pt |
| **AMBERLITE IRC748** | **IDA** | Chelating resin for metals removal |
| **DOWEX M4195** | **Bis-PIC** | Chelating resin for Copper, Nickel, and Cobalt processing. |
| **DOWEX XUS43578** | **Bis-PIC** | 410µm uniform chelating resin for Copper, Nickel, and Cobalt processing. |
| **DOWEX XUS43600** | **Thiouronium** | Special resin for recovery of Platinum Metals (PGM's). |
| **DOWEX XUS43604** | **Thiol** | Mercury Removal |
| **DOWEX XUS43605** | **HPPA** | Cu selectivy at low pH in the presence of Fe |
| **DOWEX XZ 91419** | **N-Butyl-Amina** | Large bead, gold selective strong base anion resin with t-Butylamine groups for recovery of gold from cyanidation leach solutions (manufactured under license from MINTEK) |



# Mining Industry trends impacting Water treatment needs

| Water Quality and Scarcity | Environmental Impact Driving Stricter Regulations | Lower Ore Grades | Growth of Emerging Economies impacts Commodities Prices |
|---|---|---|---|

| Water Supply | Reuse | Metal Recovery | Effluent Treatment | Brine Management |
|---|---|---|---|---|
| Water Scarcity and Poor Quality are driving demand for Desalination Projects to supply Mining sites | Water Scarcity and tougher regulations are driving demand for efficient water use/reuse | Higher Commodity prices and lower ore grades are driving recovery of metals from tailings and other waste streams | Increasing awareness of environmental impact from mining sites and stricter regulations are driving demand for Acid Rock Drainage solutions | Use of advanced technologies is creating needs for salt disposal solutions due to regulations and costs |

# Mining water and wastewater treatment

## Drivers for membrane adoption

**Technical**

- Recovery of metals
- Recovery of clean water
- Improve mining process
- Sludge generation reduction and/or elimination
- Metal fractionation

**Environmental**

- Meet waste water discharge requirements
- Dam / Tailings treatment
- Avoiding fines for noncompliance

**Social**

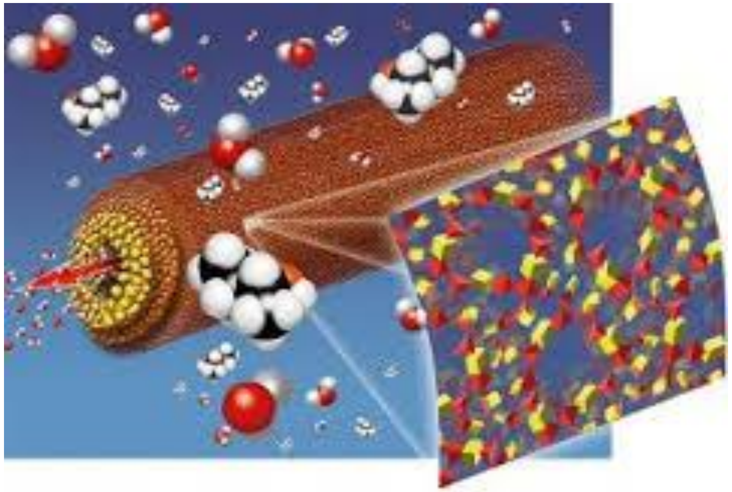
- Maintain license to Operate
- Share delicate resource: water

**Figure 3.** Mining water and wastewater market revenue forecast by segment (2011-2016)

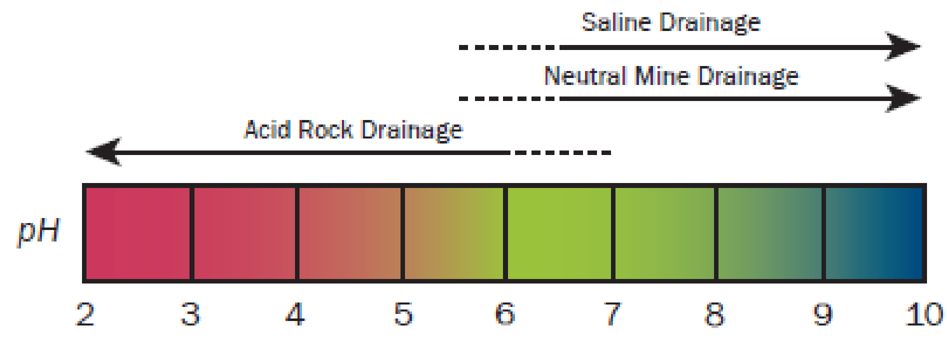

Source: GWI Report

# Case Study
## *Acid Mine Drainage water treatment utilizing Nanofiltration membranes*





# Acid Mine/Rock Drainage




*Source: GARD Guide, 2011*

**Figure 1.33 Types of drainage produced by sulphide oxidation**

| Acid rock drainage | Neutral mine drainage | Saline drainage |
|---|---|---|
| Acidic pH (2-6) | Near neutral to alkaline pH (7-10) | Neutral to alkaline pH (7-10) |
| Moderate to elevated metals | Low to moderate metals (may have elevated zinc, cadmium, manganese, antimony, arsenic or selenium) | Low metals, may have moderate iron |
| Elevated sulphate | Low to moderate sulphate | Moderate sulphate, magnesium and calcium |
| Treat for acid neutralisation, metal and sulphate removal | Treat for metal and sometimes sulphate removal | Treat for sulphate and sometimes metal removal |

**Sources**
- Tailings
- Waste rock stockpiles
- Ore and low-grade ore stockpiles
- Heap leach materials
- Pit walls
- Underground workings

→

**Pathways**
- Runoff
- Infiltration through mine waste
- Infiltration through soil/vadose zone
- Groundwater
- Surface water
- Uptake by biota
- Movement of mone waters
- Air

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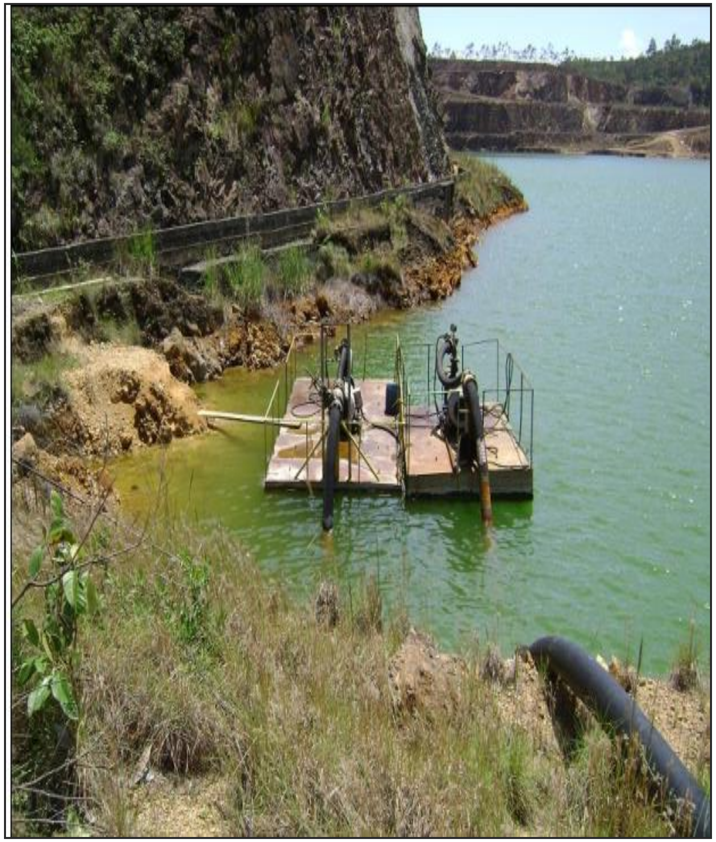
**Receiving environment**
- Groundwater
- Surface water
- Air
- Soil
- Sediment

# Case Study – *the challenge*



**Water Challenge**

- Removal of $MnSO_4$ from AMD to comply with local legislation (CONAMA 430/11)
- Meet discharge limit of Mn < 1 mg/L

**Brazil Uranium Mine**

- Situation: Clean-up (15 years operation)
- Liquid Effluent Treatment still active

**Tailings Dam**

- Exhausted
- Direct release to water source unacceptable
- Needed to adopt to meet local Legislation
- High level $Ca(OH)_2$ to precipitate sulfate
- High Level of Sulfur (pyrite Fe $S_2$)
- High Level of Manganese

# Case Study – *6 month pilot trial*



## Define membrane performance to determine long term operation and economics

- Evaluate specific membrane characteristics (targeted recoveries, fouling & scaling in harsh waters)
- Operational parameters for long term performance (pretreatment, cleaning protocol, antiscalant, etc)
- Economic analysis vs. traditional treatment

| | |
|---|---|
| Configuration | 1 stage, single pass |
| Vessels | Codeline 8" |
| Elements /Vessel | 1 |
| Type of Element | Polyamide NF |
| Manufacturer | Dow FILMTEC$^{TM}$ |
| Model | XUS 229323 |
| Feed Water | AMD, 1500 mS/cm at 25$^{o}$C |
| PreTreatment | Dual Media Filter + Cartridge Filter |
| Typical RO Feed | SDI <3 |
| RO Recovery | 9% (Avg/element) |
| Feed Capacity/Unit | 10 m3/hr |

# Case Study – *performance results*

- ***Delivered desired Sulfate & Manganese removal level to meet discharge limits (<1 mg/l).***
- ***Excellent removal of all rare earth elements to greater than 95%, except Uranium at 87%***

## Feed Water Composition

| Date | | 10-jan | 18-jan | 25-jan | 1-feb | 8-feb | 14-feb | 23-mei | 13-jun | Average |
|---|---|---|---|---|---|---|---|---|---|---|
| pH | | 3,36 | 3,56 | 3,52 | 3,56 | 3,66 | 3,54 | 3,55 | 3,65 | 3,53 |
| FEM | mV | 501,8 | 532,4 | 514,2 | 547,5 | 501,4 | 561,6 | 561,8 | 566,9 | 519,5 |
| Condutividade | µS/cm | 1.717 | 1.455 | 1.413 | 1.569 | 1.485 | 1.502 | 1621 | 1541 | 1.528 |
| U | mg/L | 5,82 | 9,6 | 6,95 | 8,7 | 8,26 | 8,49 | 7,01 | 6,41 | 7,87 |
| Mn | mg/L | 61,4 | 95,3 | 73,1 | 87,3 | 85,3 | 85 | 104 | 86 | 80,5 |
| $SO_4^{2-}$ | mg/L | 1.298 | 1.158 | 1.075 | 1.001 | 991 | 973 | 1098 | 1072 | 1.105 |
| Fe | mg/L | 3,863 | 1,2 | 0,46 | 0,703 | 0,307 | 0,79 | 0,73 | 0,28 | 1,31 |
| Ca | mg/L | 242,2 | 100,3 | 85,3 | 94,6 | 87,7 | 87,5 | 112 | 86,6 | 122,0 |
| Mg | mg/L | 9,27 | 8,02 | 6,49 | 7,73 | 7,55 | 7,41 | 9,23 | 7,62 | 7,81 |
| Si | mg/L | 11,3 | 11,45 | 14,2 | 16,3 | 14 | 12,4 | NA | NA | 13,45 |
| Al | mg/L | 122,3 | 189 | 132 | 160 | 179 | 149 | 182 | 170 | 156 |
| Na | mg/L | 1,5 | 1,8 | 1,7 | 1,9 | NA | NA | NA | NA | 1,7 |
| K | mg/L | 8,6 | 9,4 | 8,7 | 8,4 | NA | NA | NA | NA | 8,8 |
| $Cl^-$ | mg/L | 0,45 | NA | NA | NA | NA | NA | NA | NA | 0,45 |
| F- | mg/L | NA | NA | 87,7 | 93,3 | 111 | 106 | 154 | 141 | 110,4 |
| $NO_3^-$ | mg/L | 0,5 | NA | NA | NA | NA | NA | NA | NA | 0,50 |
| Zn | mg/L | NA | NA | NA | 13,9 | 13,6 | 13,4 | NA | NA | 13,8 |
| Mo | mg/L | NA | NA | NA | 0,94 | 0,9 | 0,87 | NA | NA | 0,92 |
| La | mg/L | 39,3 | 51,8 | 40,6 | 50,4 | 49,9 | 48,8 | NA | NA | 47,4 |
| Ce | mg/L | 23,39 | 27,5 | 24,3 | 27,1 | 27,4 | 26,4 | NA | NA | 26,2 |
| Pr | mg/L | 2,55 | 3,02 | 9,56 | 8,29 | 9,14 | 9 | NA | NA | 7,32 |
| Nd | mg/L | 8,57 | 11,4 | 9,7 | 12,2 | 11,7 | 11,4 | NA | NA | 11,0 |
| Sm | mg/L | 1,21 | 1,6 | 1,06 | 1,3 | 1,29 | 1,24 | NA | NA | 1,29 |
| Y | mg/L | 3,53 | 5,39 | 4,42 | 5,37 | 5,3 | 5,12 | 6,23 | 5,11 | 5,05 |

## AMD Ion Removal

| Specie | Average Removal ± RSD / % |
|---|---|
| Manganese | 98,8 ± 0,7 (n =45) |
| Fluoride | 98,1 ± 0,8 (n = 55) |
| Sulfate | 95,1 ± 0,5 (n = 48) |
| Zinc | 98,1 ± 0,1 (n =3) |
| Calcium | 97,9 ± 1,9 (n=8) |
| Aluminium | 99,1 ± 0,5 (n =8) |
| Uranium | 87,0 ± 5,0 (n =45) |

## AMD Rare Earth Recovery

| Specie | Average Removal ± RSD / % |
|---|---|
| Lanthanum | 99,5 ± 0,2 (n= 6) |
| Cerium | 99,5 ± 0,2 (n=6) |
| Praseodymium | 96,7 ± 0,2 (n=5) |
| Neodymium | 99,4 ± 0,2 (n=6) |
| Samarium | 98,4 ± 0,1 (n=6) |
| Yttrium | 99,4 ± 0,3 (n=7) |

# Case Study – *membrane surface results*

## Membrane Autopsy

- ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) was applied to the membrane to identify what element would have more probability to scale in the membrane
- Aluminum and Iron were the most prevalent metals with the most precipitation, but not at levels which intruded membrane performance

## Membrane Cleaning

- Ten CIP's conducted over 2000 hours
- Oxalic acid cleaning followed by caustic soda yielded the best results

**Extract of autopsied membrane**

| Element | mg/L |
|---|---|
| Ni | 0,145 |
| Cu | 0,06 |
| Zn | 3,34 |
| Mo | <0,004 |
| Cd | 0,015 |
| Ba | 0,134 |
| Y | <0,004 |
| La | 0,7 |
| Ce | 0,48 |
| Nd | 0,23 |
| Sm | 0,03 |
| Gd | 0,02 |

| Element | mg/L |
|---|---|
| U | 4,88 |
| Mn | 2,78 |
| $SO_4^{2-}$ | 127 |
| Fe | 12,5 |
| Ca | 6,1 |
| Mg | 2,94 |
| P | 1,27 |
| Al | 46,7 |
| Ti | 0,43 |
| V | 0,01 |
| Cr | 0,2725 |

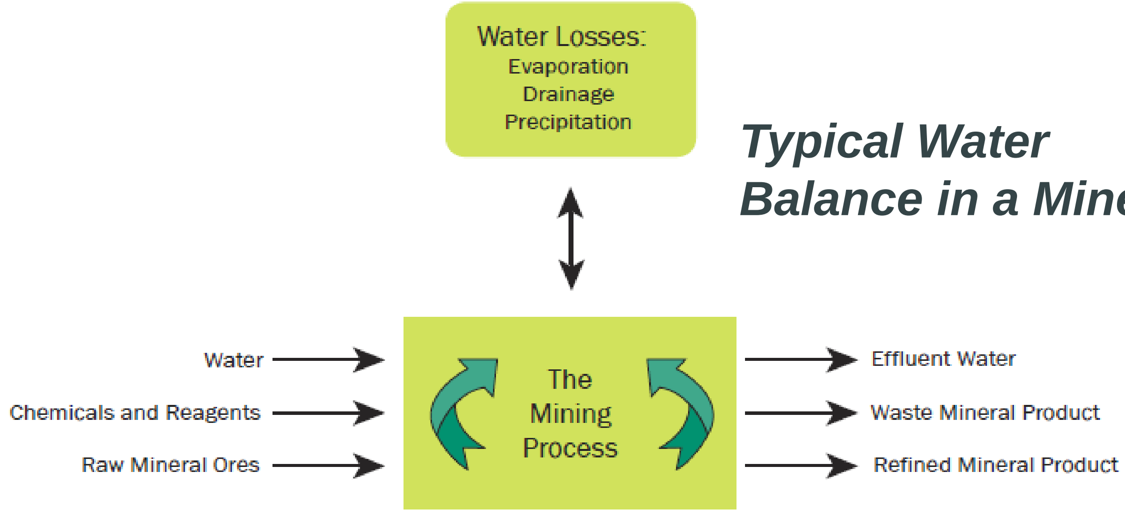
# Case Study – *conclusion*

**Acid Mine Drainage waters with high contamination can be cost effectively treated with tailored nanofiltration membranes with optimized operation protocols and the appropriate system design.**

- Reduced sulfate, manganese, and fluorine to generate permeate flow to meet local regulatory levels for disposal and or reuse (<1 mg/l Mn)
- Delivered excellent recovery of all elements as rare earths
- With proper pre-treatment and operational protocols, the lifetime of nanofiltration membranes in harsh waters can be achieved (robust, easy to clean, low fouling)
- Nanofiltration membranes have a lower footprint and can achieve a lower OPEX vs. physical chemical treatment

# Mining separation -- *challenges & adoption*

***Unique Sites require Breadth of Capabilities to develop Unique Solutions***




Source: Fleming 2011

***Typical Water Balance in a Mine***

- Water Challenges and Mining Processes vary significantly depending on the mineral being processed and the stage where water is being considered

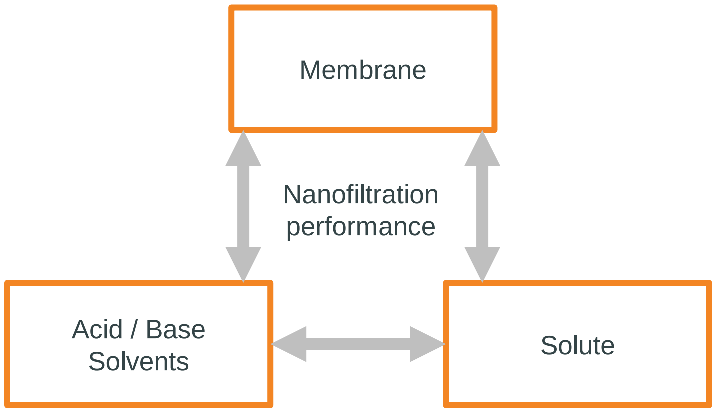
- Every mine is unique in geology, water chemistry, etc
- This requires that each mine separation solution needs to be defined holistically

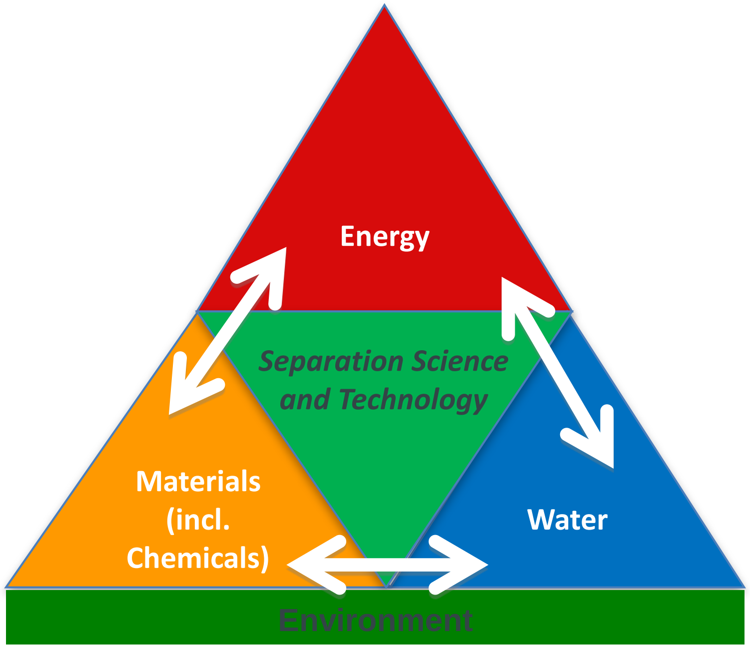
# Mining separation - *challenges & innovation*

***Innovations addressing material challenges will enable separations in increasingly harsh environments with longer membrane lifetimes***

- **Exposure to acid/base limits product lifetime**
  PA-based RO/NF membranes are susceptible to degradation

- **Exposure to solvents impairs performance**
  Conventional RO/NF/UF membranes swell



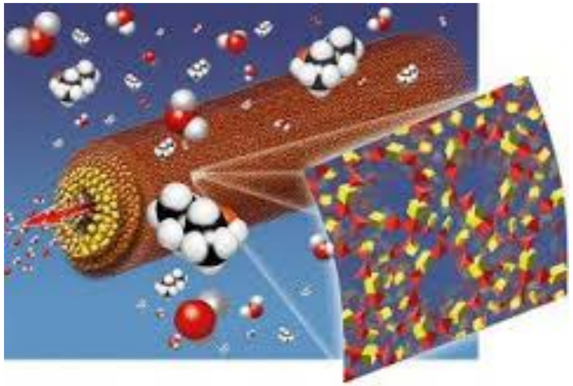

Source: ACS Separation Science and Technology (SST) as the Convergence Platform for *SusChEM*,

# A few examples….Mining Commercial applications

| Site / Year | Capacity m3/day | Scope | Application |
|---|---|---|---|
| Longyu Coal mine , China | 5.278 | UF & RO | Boiler make up from coal waste water |
| GoldFields Ghana, 2013 | 2 x 7.500 | UF&RO | Gold mine waste water |
| Anglo American Thermal Coal, New Vaal Colliery, Free State, SA. | 20.000 | UF&RO | Coal mine waste water treatment |
| Minera Collahuasi, Chile ; 2002 | | UF&RO | Make up water for copper mine |
| Minera Escondido, Chile, 2006 | 45.000 | UF&RO | Make up water for copper mine |
| Mining Mantoverde, 2012 | 10.400 (expansion to 26.000 m3/day) | UF&RO | Make up water for copper mine |
| Gold mine; Yanacocha, Peru | 72.000 | RO | Barren leach recovery of cyanide and metals |
| Cananea Mexico, 1997 | 24.000 | NF | PLS preconcentration and removal of excess wastewater |
| Kennecott Copper (Rio Tinto) 1998 | 12.000 | UF&RO | ARD wastewater treatment |
| Zijin Copper mine, Xiamen, China; 2009; | 6000 | UF&RO | ARD wastewater treatment |

# Summary

- **Nanofiltration membranes have been proven to deliver cost effective performance within Acid Mine Drainage and Mining water management today.**
- **Adoption & Innovation will foster new solutions**
- **Membrane technology has intrinsic advantages vs. alternative separation technologies to meet even broader purification and separation challenges**
  - Critical Materials & Mining waste water and metals recovery
  - Novel chemistries will be needed to meet material performance challenges to enable separations in these increasingly difficult environments


# Thank You

# Nanofiltration / Reverse Osmosis

Spiral Wound Configuration

- 2,5 - 4 – 8 - 16” diameter 40”length
- Operated at 5 – 80 bar
- Per element with 37m$^2$
  - NF- 55 m$^3$/day at 5 bar
  - BW- 40 m$^3$/day at 15 bar
  - SW- 25 m$^3$/day at 55 bar