Control and Prevention of ARD with Thiocyanate

Dr. Gregory J. Olson

Little Bear Laboratories, Inc., Golden, Colorado

Control and Prevention of ARD with Thiocyanate

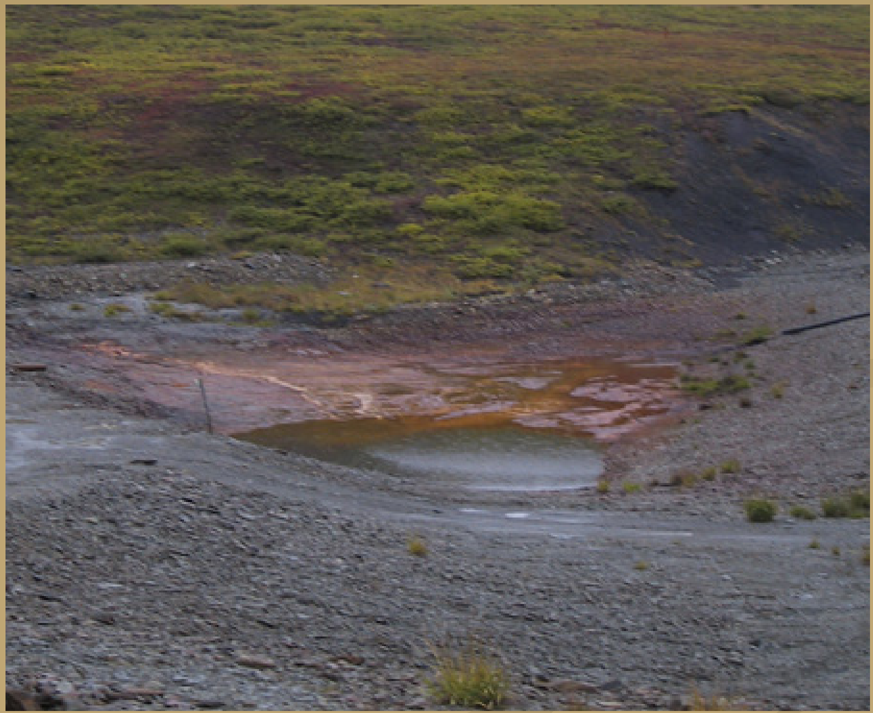
Gregory J. Olson and Thomas R. Clark, Little Bear Laboratories, Inc., Golden, Colorado

Terry I. Mudder, TIMES, Ltd., Sheridan, Wyoming

Mark Logsdon, Geochimica, Inc., Ojai, California

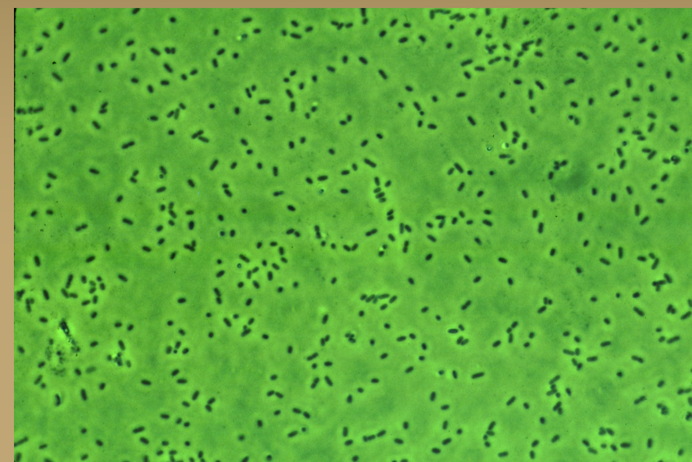
Biooxidation of Sulfides and ARD

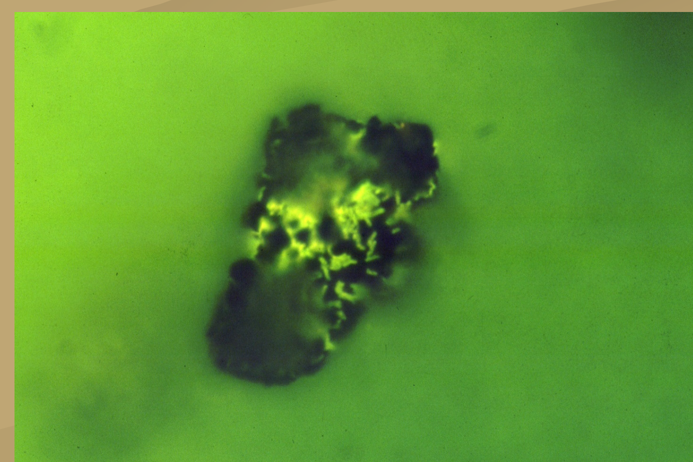
- Pyrite oxidized by O_2, more rapidly by Fe^{3+}
- Fe biooxidation more important than abiotic Fe oxidation at pH <5 (Kirby et al., 1999)
- S^o biooxidized to H_2SO_4
- Inhibiting Fe- and S-oxidizing microorganisms reduces ARD in proportion to microbial role in ARD formation



Agents Inhibiting Pyrite Oxidizing Bacteria

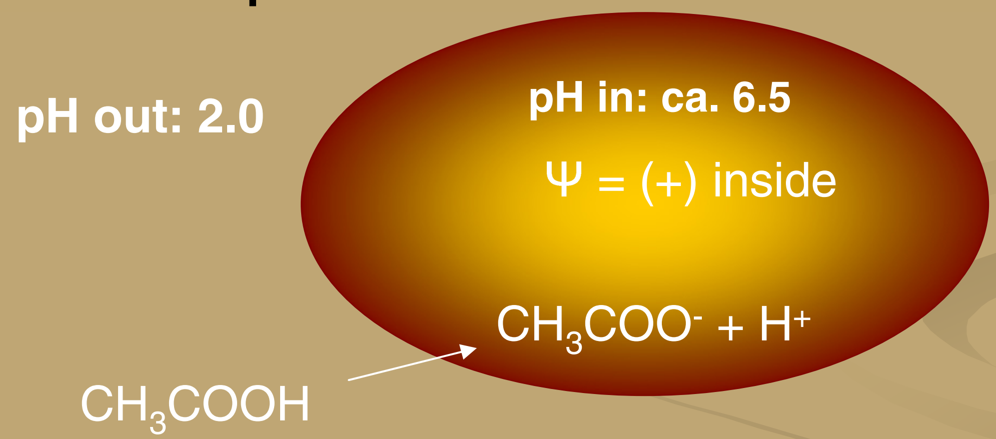
- Surfactants (SLS): disrupt membranes
- Organic acids (e.g., acetate)
- Certain metal(loid)s: Hg, Ag, As(III)
- Certain anions (Cl^-, F^- NO_3^-, SCN^-)
- Low-level SCN^- has resulted in biooxidation process failures





Mechanism of Action of Agents Inhibitory to Acidophiles: Organic Acids and Anions

Toxicity of organic acids and lipophilic anions (SCN^-, NO_3^-) is a consequence of the unique physiology of acidophiles:



$S^{14}CN^-$ used as a probe of membrane potential, ψ

Thiocyanate as a Biocide for ARD Prevention and Control: Attributes

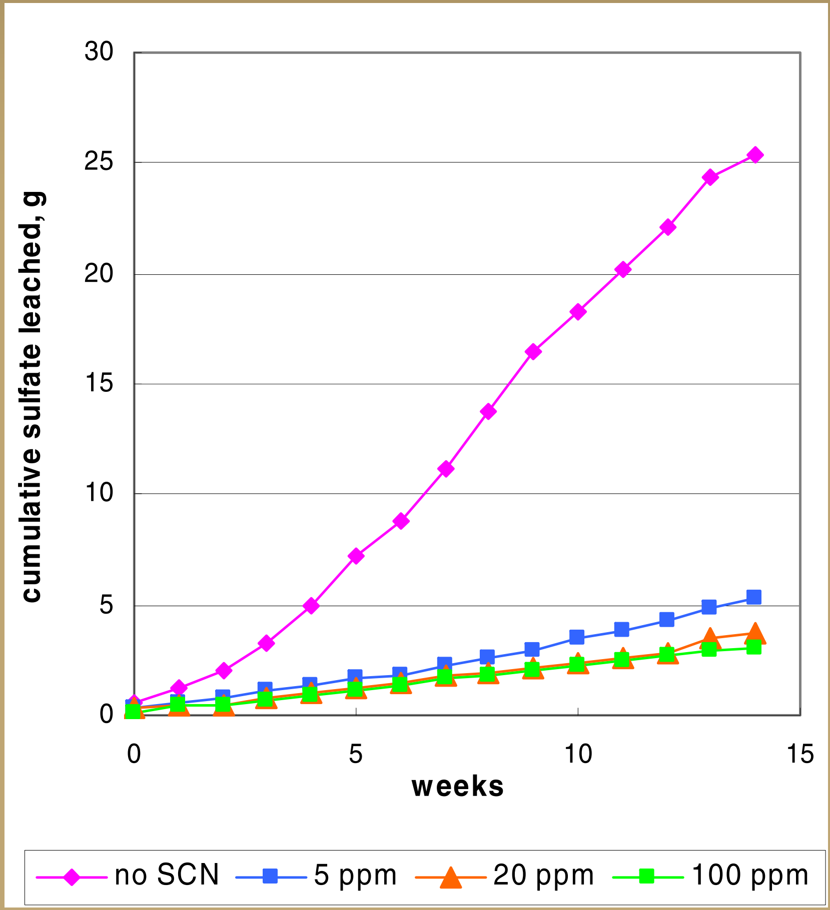
- Highly and selectively toxic to acidophiles
- Relatively non-toxic to other organisms
- Relatively stable in acidic environments
- Relatively low binding to rock
- Biodegradable in “normal” environments
- Commercially available and inexpensive
- Component of process solutions at precious metal mining operations

SCN Inhibition of ARD: Lab Accelerated Weathering Tests

25 KG SCALE

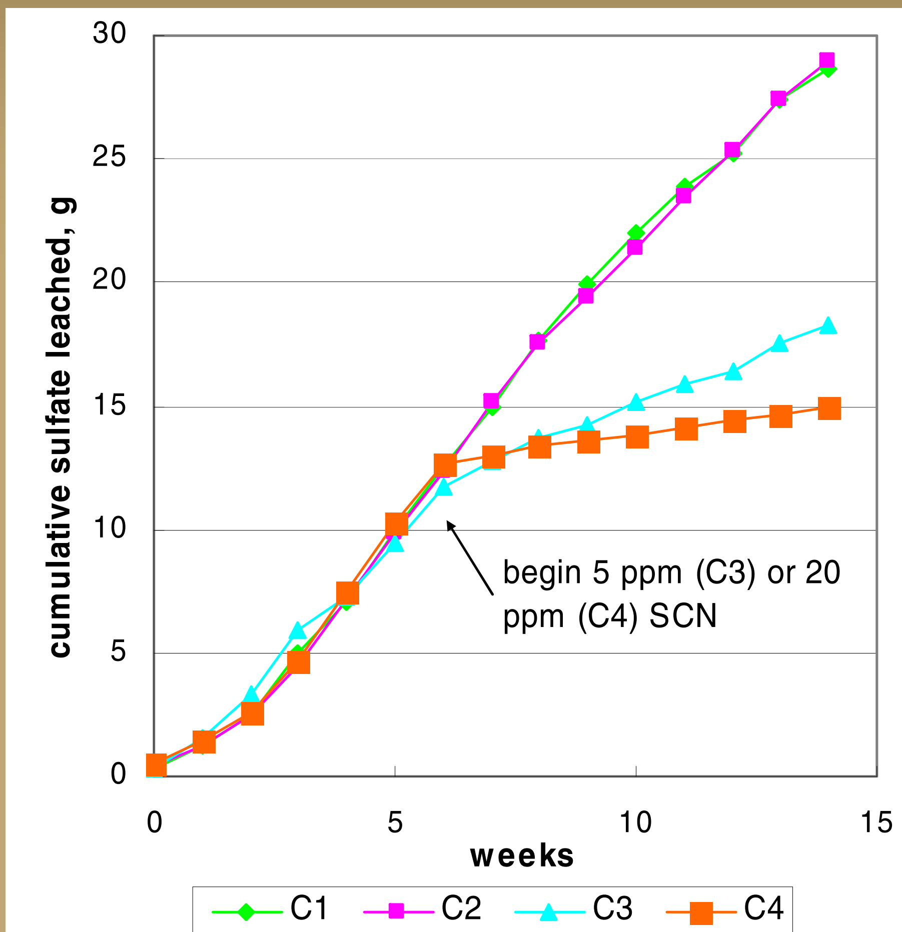
Thiocyanate Prevents Biocatalyzed ARD:

Weekly Application H_2O to Waste Rock 1kg Humidity Cells



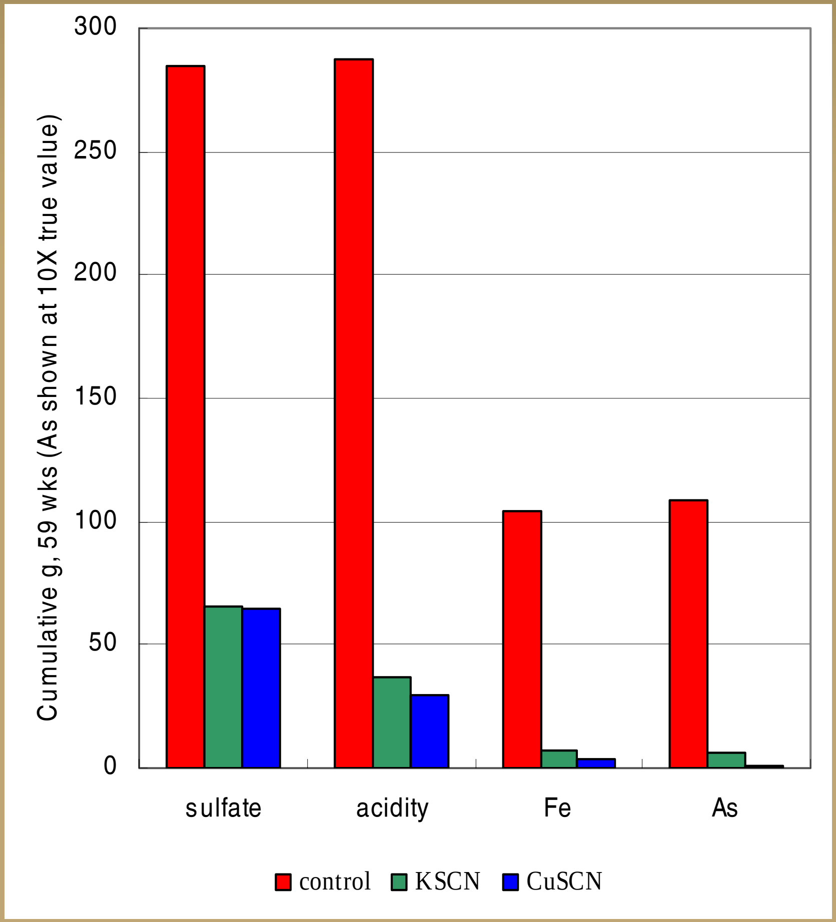
- 5 ppm SCN reduced SO_4 production rate 85% when applied to 3% sulfide waste rock
- 100 ppm SCN reduced SO_4 production rate 91%
- SCN kept ARD near the abiotic (O_2) background rate

Thiocyanate Controls Biocatalyzed ARD:
Begin SCN Application to Waste Rock After 6 Weeks



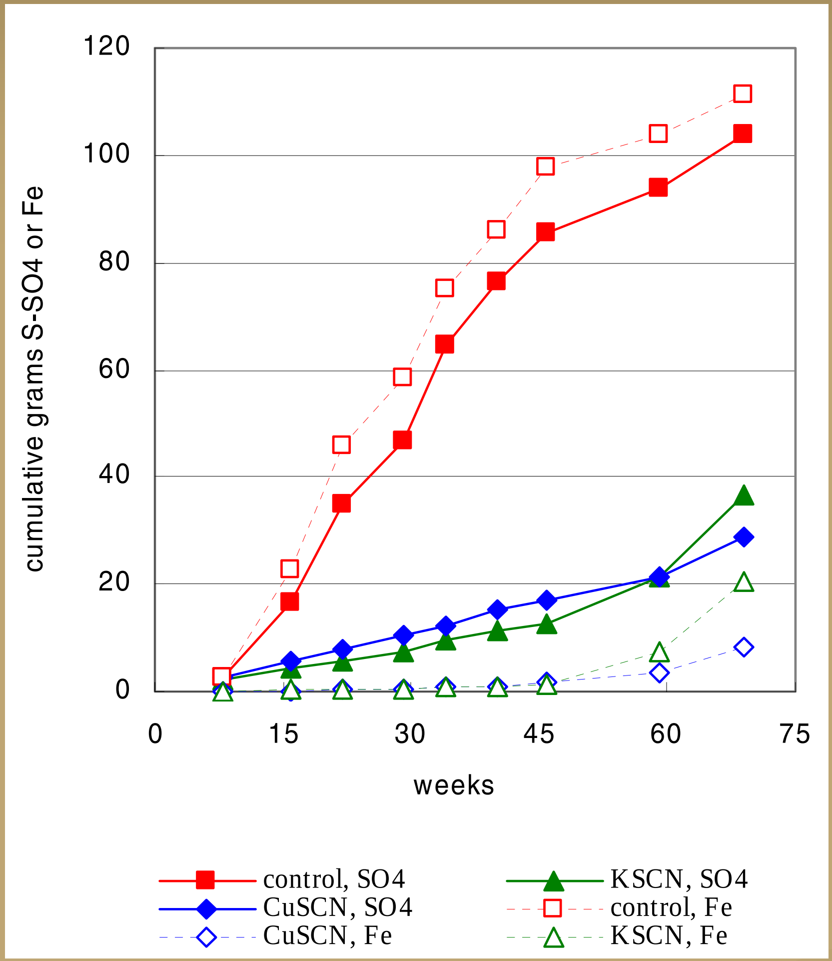
- 5 ppm SCN added after 6 wks, ARD rate reduced 55%
- 20 ppm SCN after 6 wks, ARD rate reduced 87%
- SCN somewhat less efficient when added to actively biooxidizing sulfidic waste rock

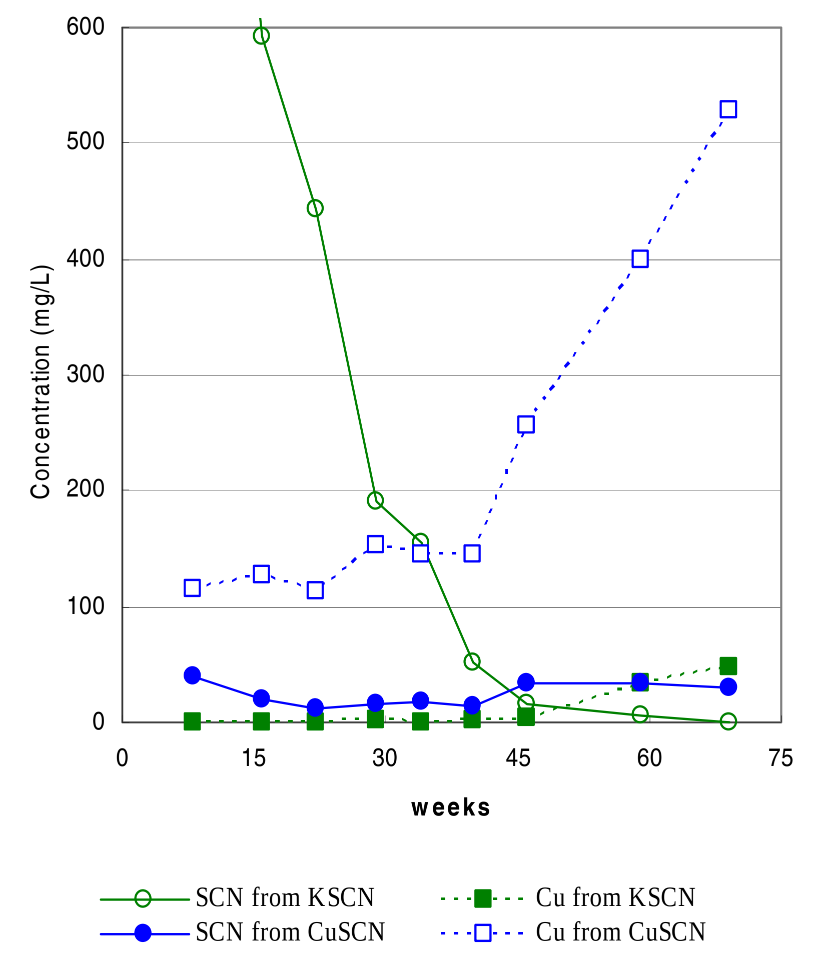
ARD Reduction with SCN: Carlin-type pyritic gold ore



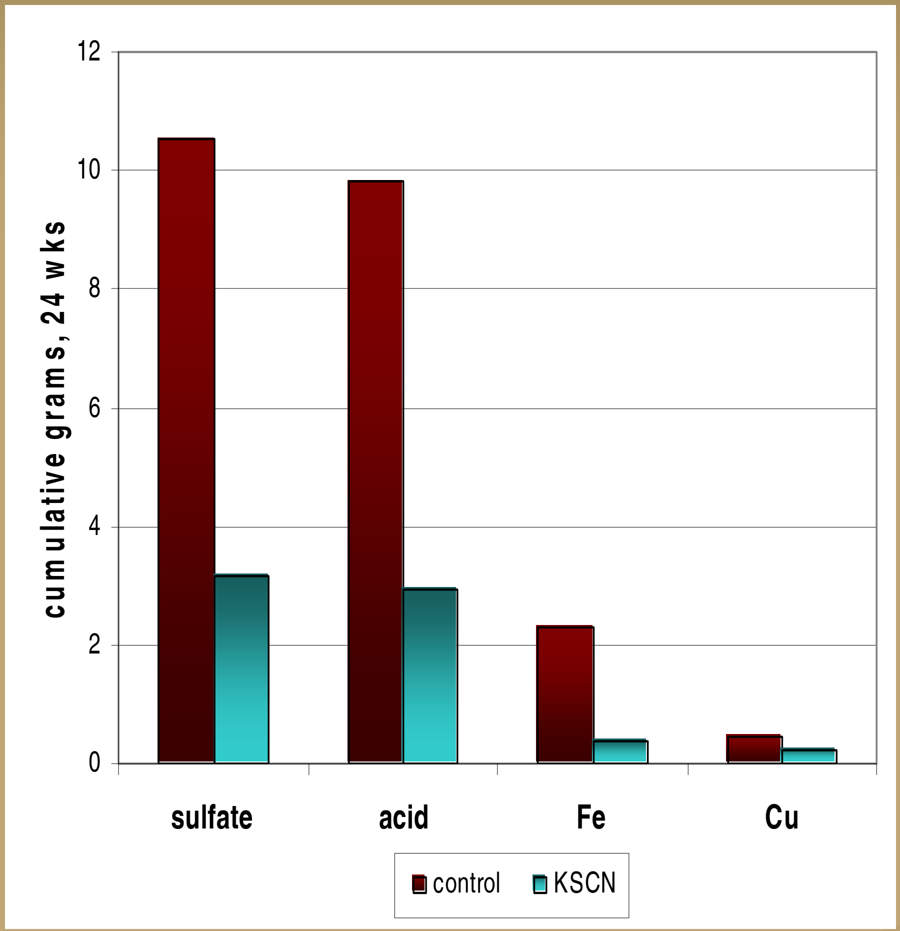
- 25 kg, ½" ore, 1.9% S
- KSCN and CuSCN added at T_0 at 200 mg SCN/kg
- 1 to 1.5 L H_2O applied once per 4 to 8 wks
- Reductions with SCN:
  - Sulfate: 78%
  - Acidity: 87%-90%
  - Fe: 93%-96%
  - As: 95%-99%
- Few ppm NH_3 in SCN-treated humidity cells

Advantages of Slow Release: CuSCN retains effectiveness





ARD Reduction with SCN: Porphyry Copper Tailing, SW U.S.



- P_{95} 28 mesh, 1.81% sulfide-S, 1 kg scale
- KSCN at T_0: 150 mg/kg
- 0.25L H_2O: 12, 24 wks
- Reductions with SCN:

  sulfate: 70%

  acidity: 70%

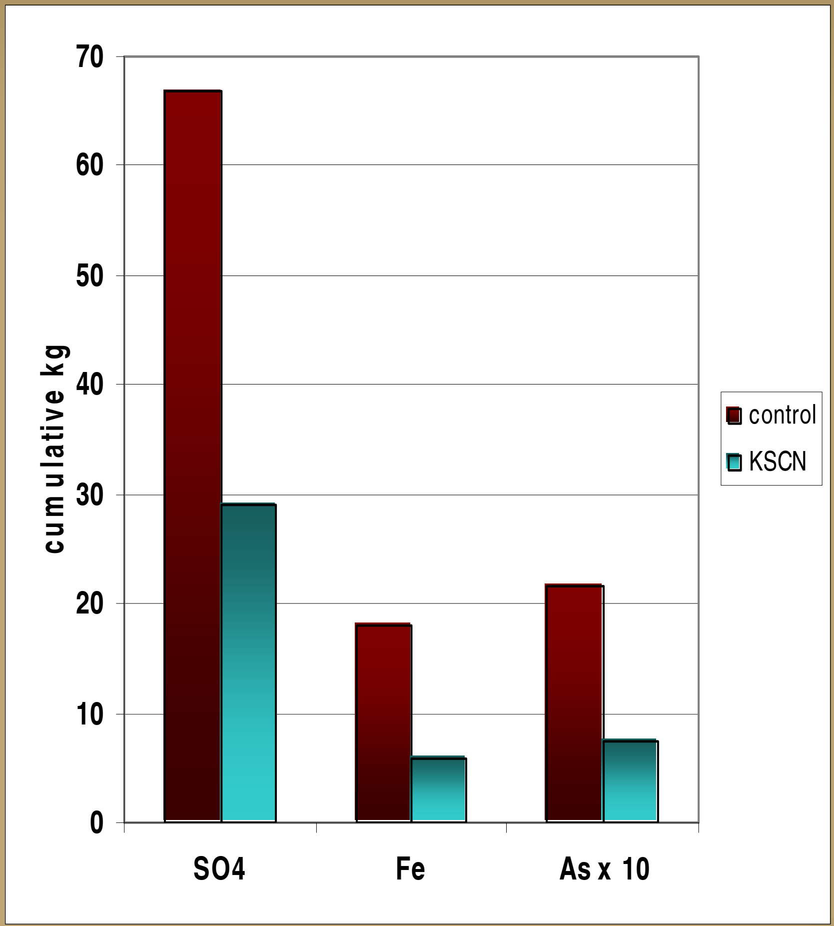
  Fe: 83%

  Cu: 41%

Mine-Site Tests: Large Columns

- 13.6 tonnes Carlin-type sulfide (1.9%) ore
- 57 mg SCN/kg at T_0
- H_2O applied monthly for 6 mo. (total 2000 L)
- Barrick Gold performed test and analyses

ARD Reduction from Carlin Ore with SCN: 13.6 tonne test



- August-February
- Reductions with SCN

  $SO_4^{=}$: 56%

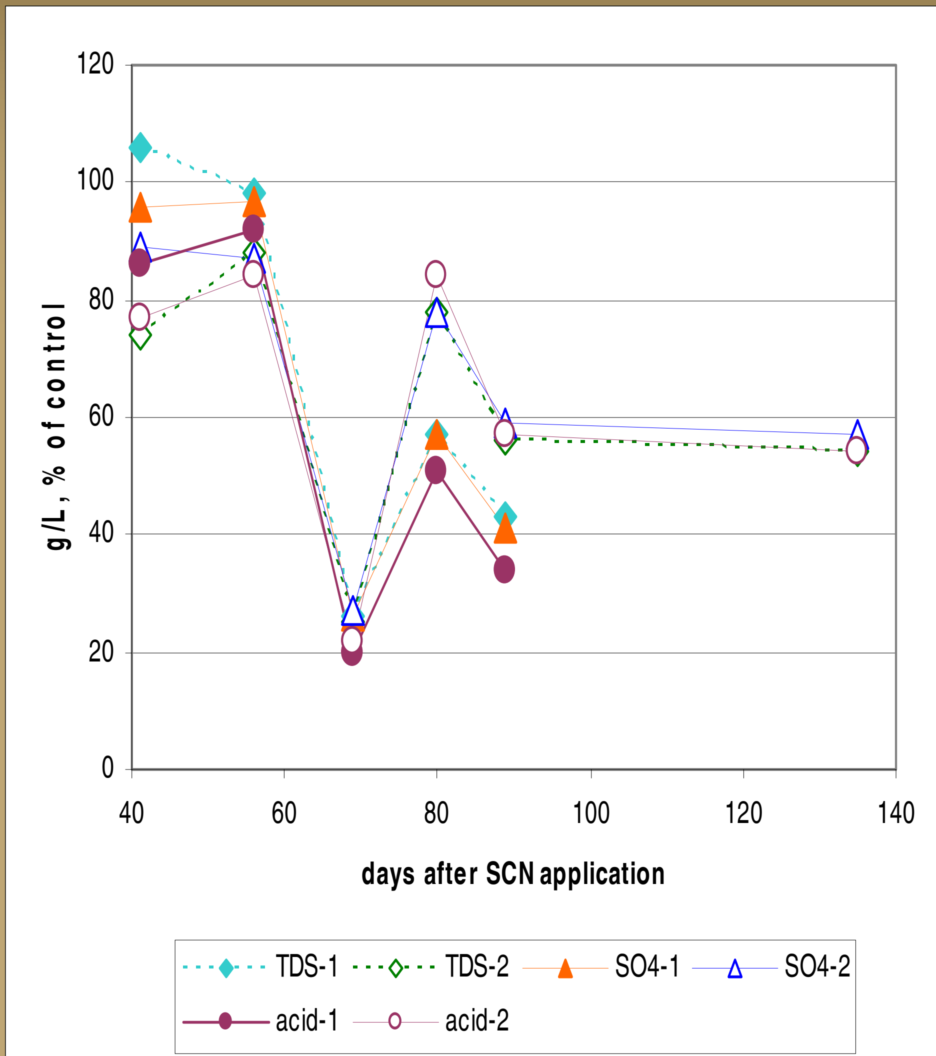
  Fe: 68%

  As: 66%
- Differences from lab: ore particle size, temperature, dose

Mine Site Tests: Waste Rock at 100 Tonne Scale

- Red Dog Mine-Alaska
- Teck Cominco performed tests
- 8m x 8m x 1.5m pits
- High S waste rock
- 1 Control, 2 SCN-dosed pits
- T_0 dose 25 mg/kg
- Rainfall leach only

100 tonne scale results



- Lag in ARD reduction: due to salts washout/ test pit operation?
- Mean % reductions day 69-135:

  TDS: 47% to 58%

  SO4: 45% to 59%

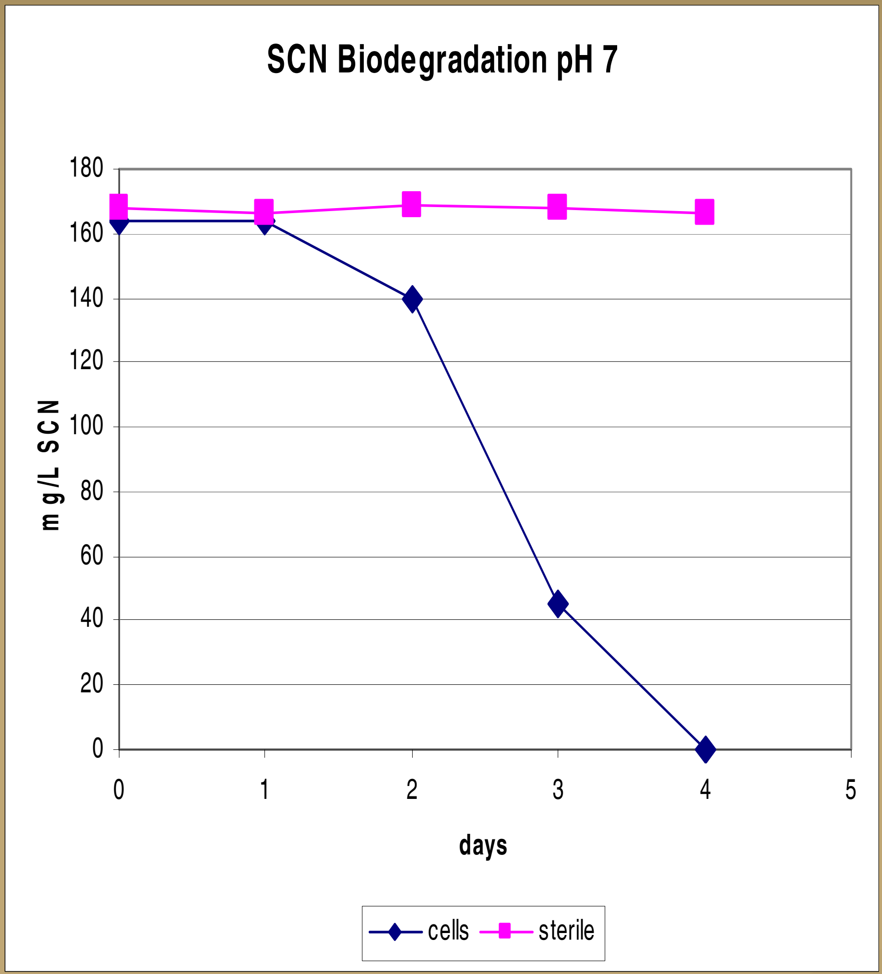
  Acidity: 46% to 65%

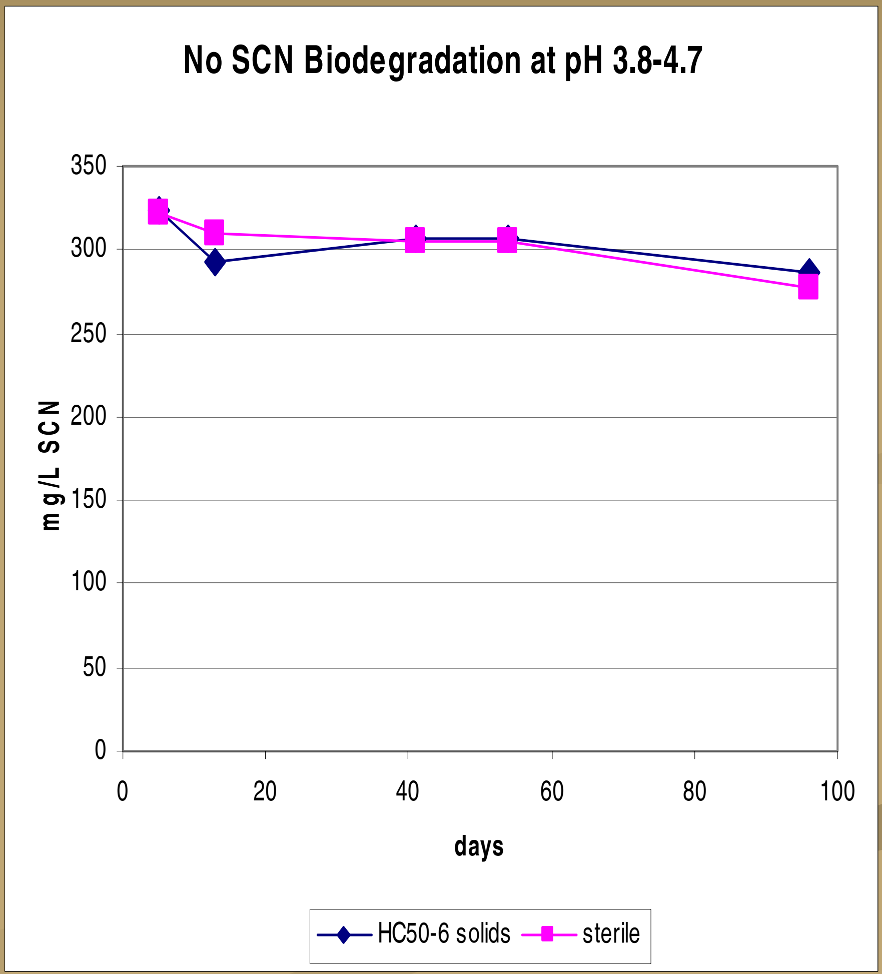
  Zinc: 43% to 53%
- NH_3 in SCN pits (ppm)
- Lab reductions: Zn 48%, acidity 55%, SO_4 65%

Fate of Thiocyanate/ Stability at Low pH

- No published reports of SCN resistance, biodegradation at low pH (<4)
- Sobolewski (1993): coal columns show SCN conversion to ammonia (no microbial study done, pH in upper zone of columns?)
- Carter (2002): patent on method to develop microbial resistance to SCN. Data are inconclusive

SCN Biodegradation:
Rapid at pH 7, None at pH 3.8 to 4.7

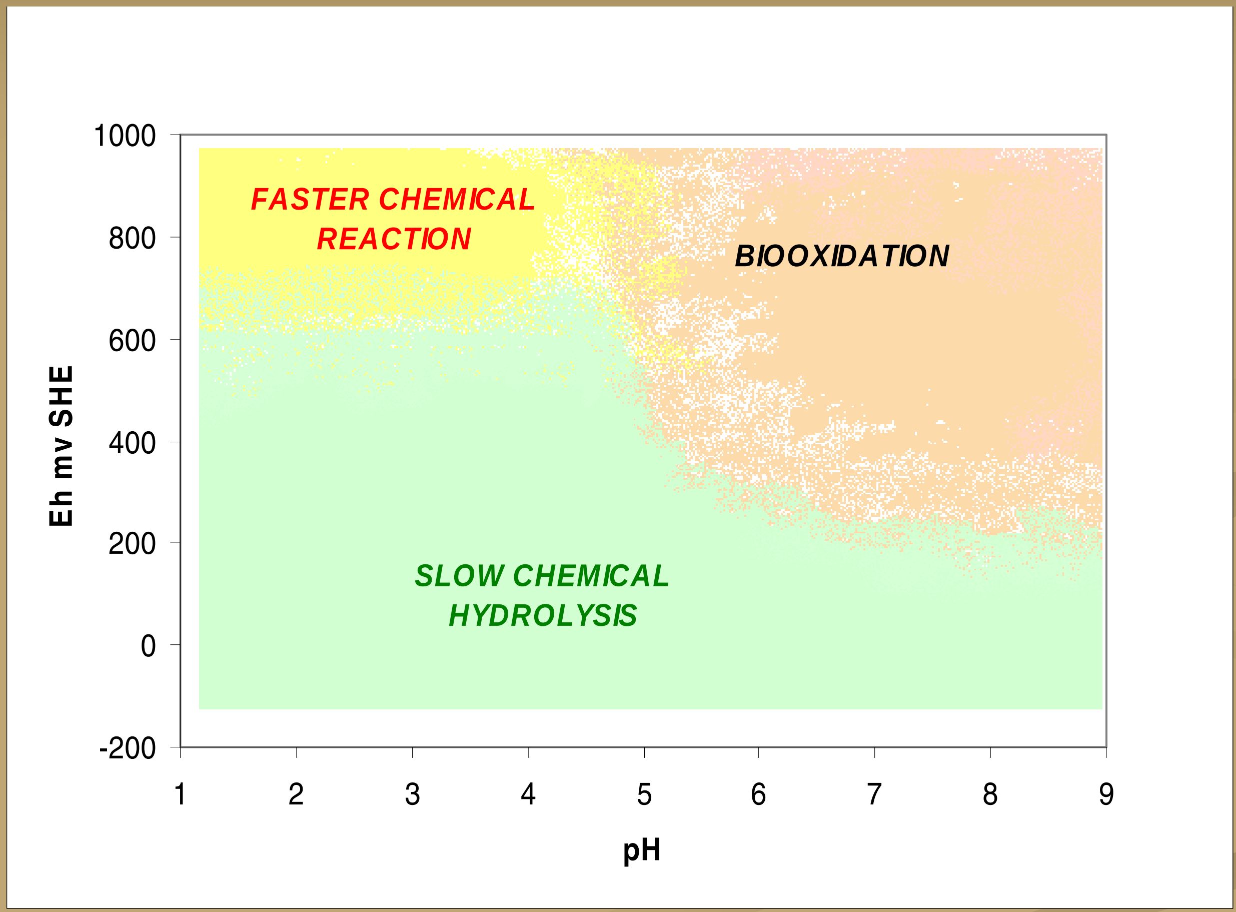




Attempts To Adapt Microorganisms To Low Concentrations Of SCN

- SCN above 10 mg/L inhibitory to Fe biooxidation; previous exposure to SCN notwithstanding. S^o biooxidation similarly affected.
- Cells grown at low SCN concentration fail to adapt significantly to SCN.
- No evidence of SCN biodegradation in columns containing SCN-pretreated sulfide ore at pH 2.6-3.
- Slow degradation of SCN is consistent with abiotic “autoreduction” of Fe-SCN complexes, producing ammonia (Barbosa-Filho and Monhemius, 1994).

SCN Stability Toward Chemical & Biological Degradation

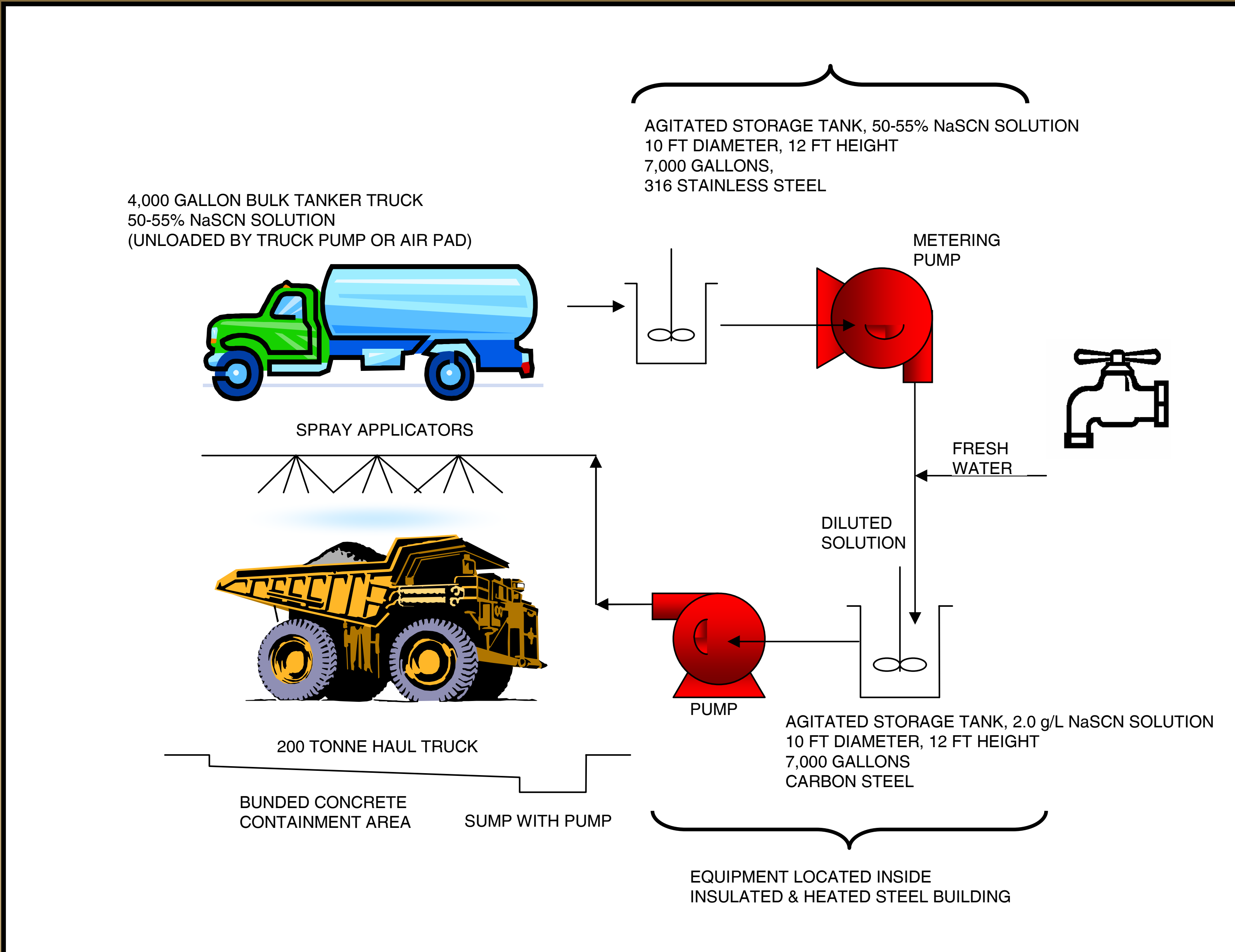


Thiocyanate Application in Mining Situations at Full Scale

- NaSCN can be purchased in 50%-55% solution or 50 lb bags at $1.40/lb; cheaper on ton basis ($0.64/lb). 70 ppm dose = $0.10 to $0.22/tonne waste rock
- CuSCN: a component of antifouling paints
- Thiocyanate a component of certain process solutions
- Thiocyanate in heaps at closure: rinse or hold?

Full-Scale Application of Thiocyanate to Freshly Generated Waste Rock

- Hypothetical open pit mine--25,000 tpd
  - 10,000 tpd acid-generating waste rock
  - 10,000 tpd non-acid generating waste rock
  - 5,000 tpd ore
- Bulk, concentrated liquid NaSCN brought to the mine
- NaSCN diluted and applied to each truck load of waste rock, 25g SCN/tonne


AGITATED STORAGE TANK, 50-55% NaSCN SOLUTION
10 FT DIAMETER, 12 FT HEIGHT
7,000 GALLONS,
316 STAINLESS STEEL
4,000 GALLON BULK TANKER TRUCK
50-55% NaSCN SOLUTION
(UNLOADED BY TRUCK PUMP OR AIR PAD)
METERING
PUMP
SPRAY APPLICATORS
FRESH
WATER
DILUTED
SOLUTION
PUMP
AGITATED STORAGE TANK, 2.0 g/L NaSCN SOLUTION
10 FT DIAMETER, 12 FT HEIGHT
7,000 GALLONS
CARBON STEEL
200 TONNE HAUL TRUCK
BUNDED CONCRETE
CONTAINMENT AREA
SUMP WITH PUMP
EQUIPMENT LOCATED INSIDE
INSULATED & HEATED STEEL BUILDING

Estimated Capital and Operating Costs
Hypothetical 25,000 tpd mine

- Estimated construction costs: $334,000
- Estimated annual operating cost: $596,000
- Total costs over 20 year mine life $12 million

NaSCN comprises 62% of operating cost

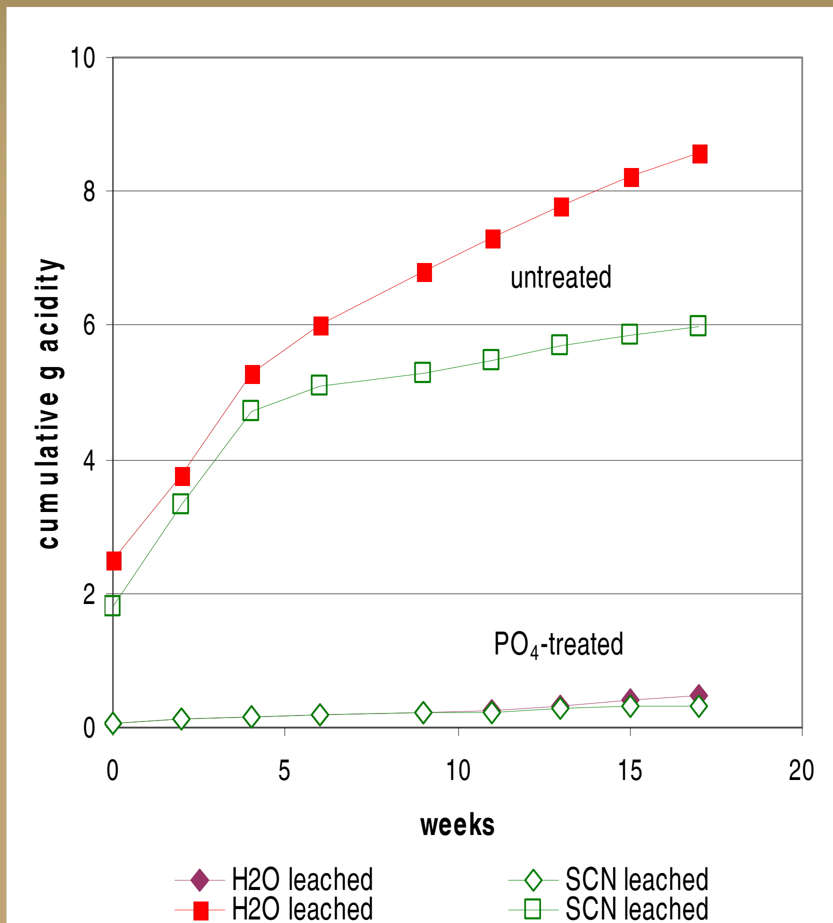
Stopping the Abiotic Component of ARD

- Biotic and abiotic oxidation of sulfides must be stopped for a comprehensive ARD solution
- Coating/encapsulation technologies have been tested: Si, Mn, PO_4
- No available technology addresses inhibition of both chemical and biological reactions for control of ARD at the source

Advantages of Phosphate

- Precipitates Fe(III) as $FePO_4$, coating surfaces and removing Fe(III) oxidant
- Neutralizes acidity, precipitates Fe and Al in non acid generating reactions
- Phosphate a powerful base, neutralizing 3X the acidity of equivalent molar amounts of lime or caustic
- Phosphate rock is inexpensive and abundant; consider also consolidated phosphate clay wastes
- Phosphate coatings labile in severe ARD (Fytas et al., 2000)—their performance could be enhanced with SCN co-treatment to stop microbial component?

ARD Control: Treatment of Oxidizing Carlin-Type Sulfidic Ore with PO_4 Solution



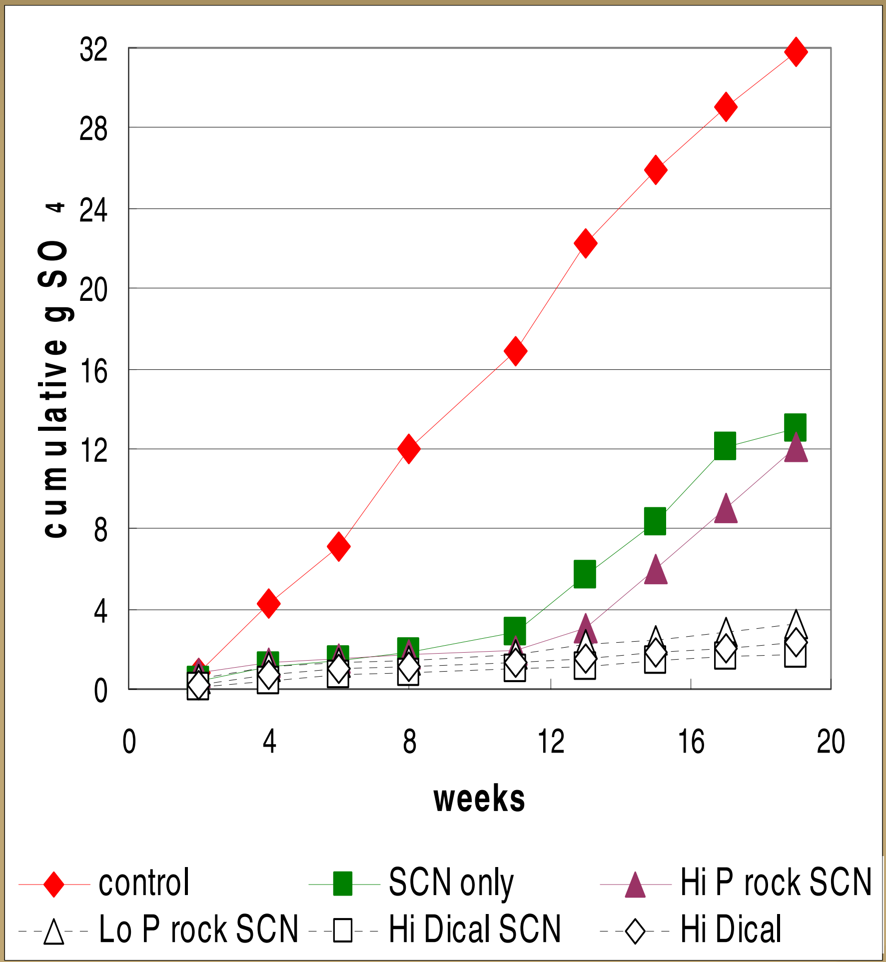
- Oxidizing ore leached with Na_3PO_4 until neutral (pH 6.2) effluent (0.94 g PO_4/kg)
- Rinse ore, load humidity cells
- Leach with water or SCN solution
- Week 4 to 17 ARD reductions:

SCN: 61% (to the abiotic oxidation rate?)

PO_4 treatment: 91%

PO_4 + SCN: 96%

Prevention of ARD: Blending Fresh Ore with Solid PO_4 + SCN



- Ore blended with 2 or 10 g/kg PO_4 and/or 200 mg/kg SCN
- Leach with water only
- 90% to 95% ARD reduction with Dical, Dical + SCN, and low dose PO_4 rock + SCN

Summary and Conclusions

- Thiocyanate at low doses stops sulfide biooxidation
- % reduction in ARD with SCN reflects the microbial role in sulfide oxidation
- SCN in mine site tests reduced ARD about 50% to 70%
- No evidence of SCN-resistant microbes or SCN biodegradation at pH <4
- SCN not a stand-alone ARD solution; useful as a part of a combined treatment

Summary and Conclusions (con't)

- SCN-containing process solutions a potential resource (pad rinsing/treatment)
- Relatively low toxicity, but potential impacts still require site-by-site evaluation
- Initial results show PO_4 is a promising co-treatment with SCN, additional test work is needed
- Ongoing efforts:
  - Larger scale/longer term PO_4 + SCN tests
  - Additional field trials planned

Acknowledgments

- U.S. Environmental Protection Agency-SBIR program
- Teck Cominco, Ltd.
- Barrick Gold, Inc.
- Homestake Mining Co.
- Phelps Dodge Mining Company