D.4 Geochemistry of Molybdenum Leaching at British Columbia Copper and Molybdenum Mines

Stephen Day, Kelly Sexsmith,
Rob Bowell and Daryl Hockley

SRK Consulting

Geochemistry of Molybdenum Leaching at British Columbia Copper and Molybdenum Mines

Stephen Day, Kelly Sexsmith,
Rob Bowell, Daryl Hockley

Presented at 7th Annual BC Metal Leaching/ARD Workshop, November 29 and 30, 2000

SRK

Acknowledgements

- Highland Valley Copper (Mark Freberg)
- Thompson Creek Mining – Endako Mines Division (Barb Riordan)

SRK

Presentation Outline

- Geological Setting of BC Deposits
- Primary and secondary Mo minerals
- Current understanding of Mo geochemistry
- Mo geochemistry at two BC Mines
- Performance and limitations of MINTEQA2 databases

SRK

Geological Setting

- Mo - Endako, Kitsault, Brenda.
- Cu, Mo - Huckleberry, Kemess, Island Copper, Highland Valley, Gibraltar.
- Calc-alkaline Mo stockworks.
- Calc-alkaline porphyry.
- Variable sulphidization.

SRK

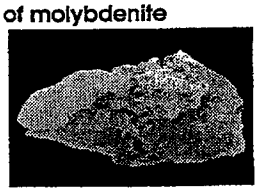
Molybdenum Sulphide Mineralogy

- Molybdenite (MoS_2)

SRK

Molybdenum Oxide Mineralogy

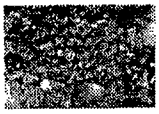
- Ferrimolybdite ($Fe_2(MoO_4)_3 \cdot 8H_2O$)
  - A soft canary yellow alteration product of molybdenite



SRK

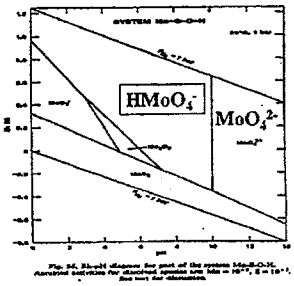
Molybdenum Oxide Mineralogy

- Powellite ($CaMoO_4$)
- Wulfenite ($PbMoO_4$)



- Molybdite (MoO_3)

Mo-S-O-H Eh-pH Diagram

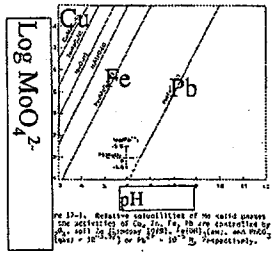


Brookins (1988)

Molybdenite Oxidation

- $MoS_2 + 9/2O_2 + 3H_2O \rightarrow$
  $2SO_4^{2-} + MoO_4^{2-} + 6H^+$
- **Molybdenite is very resistant to bacterial oxidation (MEND 1.11.1)**

Solubility of Secondary Minerals



Rai and Zachara (1984)

Solubility of Secondary Minerals

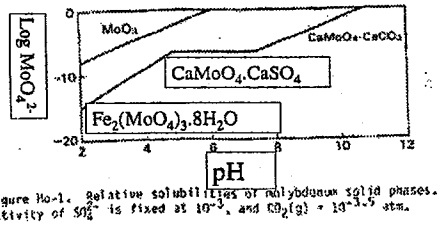


Figure Mo-1. Relative solubilities of molybdenum solid phases. The activity of SO_4^{2-} is fixed at 10^{-3}, and $CO_2(g) = 10^{-3.5}$ atm.

Rai (1987)

Summary of Mo Geochemistry

- Forms oxyanions of which MoO_4^{2-} is probably dominant
- In Fe-rich, acidic oxidizing environments, $Fe_2(MoO_4)_3 \cdot 8H_2O$ is expected to form.
- In calcareous non-acidic oxidizing environments, $CaMoO_4$ is expected to form.
- $PbMoO_4$ is the least soluble molybdate.
- Molybdate is readily adsorbed (lower pHs)

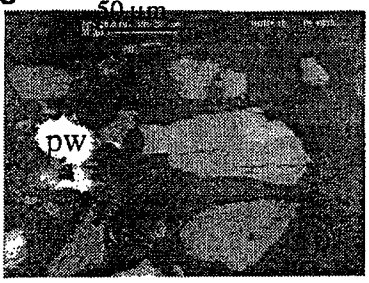
Case Example 1 – Highmont Tailings

- Highmont Mine produced Cu and Mo between 1981 and 1984.
- Tailings deposited in ring impoundment.
- Very low sulphide in tailings (<0.1%)

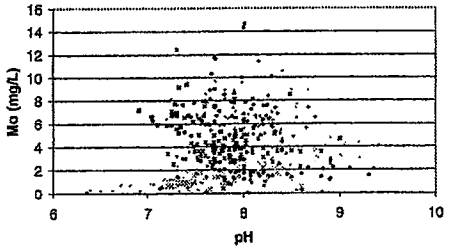
Mo Mineralogy of Highmont Tailings

- Sulphide
  - Molybdenite
- Oxides
  - Powellite ($CaMoO_4$)
  - Ilsemannite ($Mo_3O_8.nH_2O$)
  - Scheelite-powellite ($Ca[W,Mo]O_4$)
  - ?Ferritungstite ($CaFe^{3+}MoO_5OH.H_2O$)

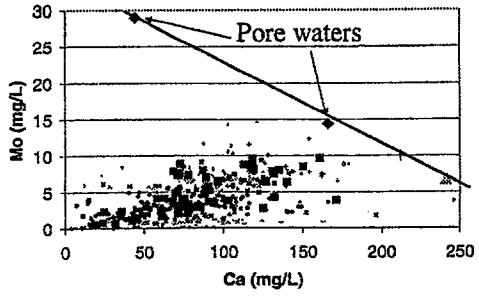
Highmont Tailings - $CaMoO_4$ in Tailings



Highmont – Mo(pH) Tailings Seeps



Highmont – Mo(Ca)



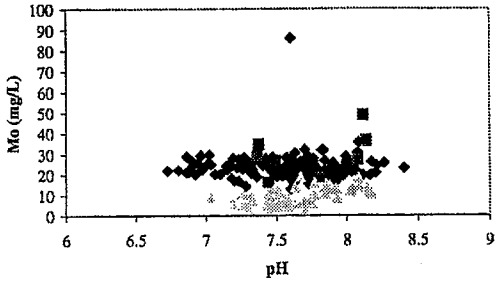
Highmont - Comments

- Mo concentrations positively correlated with Ca for individual sources.
- Highest Mo concentrations are negatively bounded by Ca for whole dataset.

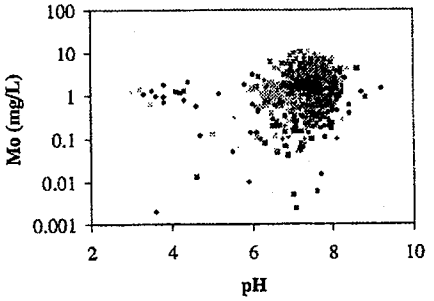
Case Example 2 – Endako Mines

- Open pit mine operated since 1970s.
- Water quality monitoring database for waste rock seepage, tailings seepage, pit seeps and small lake.
- Dominantly low sulphide (<1%), weakly calcareous (<50 kg $CaCO_3$/t) non-acid generating rock.
- Ferrimolybdite is observed.

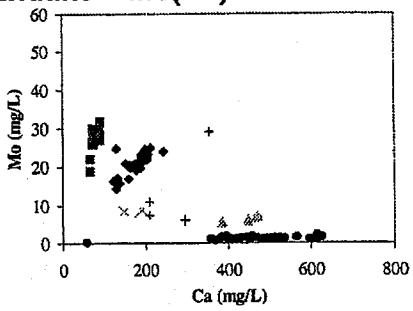
Endako – Mo(pH), Pit Waters and Waste Rock



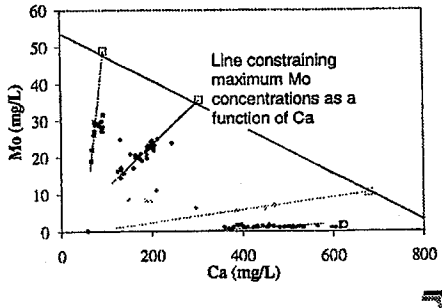
Endako – Mo(pH), Tailings Waters



Endako – Mo(Ca) – All Waters



Endako – Mo(Ca) – All Waters



Endako - Comments

- Mo concentrations positively correlated with Ca for individual sources.
- Highest Mo concentrations are negatively bounded for whole dataset (High Mo, Low Ca (Pit Water); and Low Mo, High Ca (Tailings Seeps))

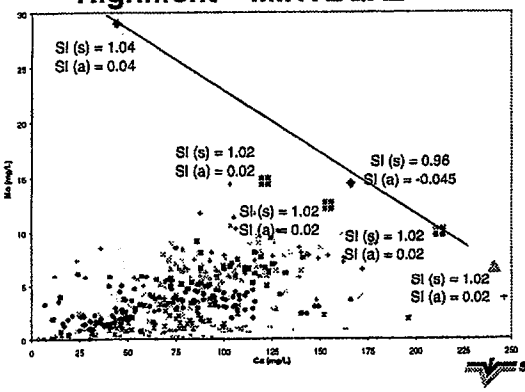
Application of MINTEQA2

- MINTEQA2 applied with thermodynamic datasets using Nordstrom (1990) with Mo data from Rai and Zachara (1984)
- Solids phases include
  - Molybdates – Fe^{3+}, Ca, Mg, Sr, Mn, Ba
  - Oxide – Molybdite
  - Molybdic Acid
- Recent MINTEQA2 release contains some similar Mo species

MINTEQ - Comparison of Log K's

Molybdate	R&Z 84	MINTEQ 2000	MINTEQ 2000 Ref
Pb	15.8	15.6	NIST46.4
Fe^{II}	7.7	10.1	Bard et al 1985
Fe^{III}	13.4	na	
Ca	7.9	8.0	NIST46.4

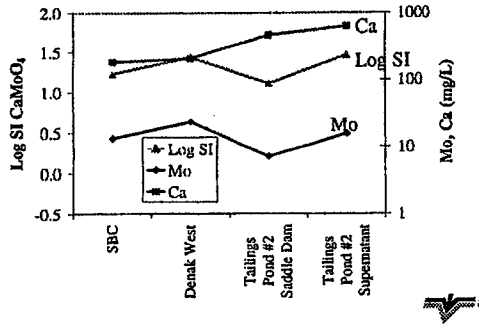
Highmont – MINTEQA2



Endako – Application of MINTEQ

- Limited by availability of Ca and alkalinity data
- Assumed calcite present

Endako – Application of MINTEQ



$CaMoO_4$ Solubility - Log K's

- Published Databases: Log K = 7.9
- Highmont: Log K = 6.9
- Endako: Log K = 6.5

- Explanations
  - Amorphous $CaMoO_4$?
  - Solid solutions?
  - Kinetics of formation (inhibitors)?

Conclusions

- Under neutral pH conditions, $CaMoO_4$ is probable solubility control.
- Published thermodynamic data under-estimate the solubility of calcium molybdate

SRK

Geochemistry of Molybdenum Leaching at British Columbia Copper and Molybdenum Mines

Stephen Day, Kelly Sexsmith, Rob Bowell, Daryl Hockley
SRK Consulting

Presented at 7th Annual BC Metal Leaching/ARD Workshop, November 29 and 30, 2000.

Reference List

Bard, A.J., R. Parsons, and J.Jordan (eds.) (1985) Standard Potentials in Aqueous Solution. International Union of Pure and Applied Chemistry, Marcel Dekker, Inc., New York, 834p.

Brookins, D.G. 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag. 176p.

HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. 1999. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0. Prepared for US EPA.

MEND 1991. Critical Literature Review of Acid Drainage from Waste Rock. Prepared by Northwest Geochem.

Nordstrom, D.K., L.N. Plummer, D. Langmuir, E. Busenberg, H. May, B,L. Jones, and D.L. Parkhurst (1990) Revised chemical equilibrium data for major water-mineral reactions and their limitations. In: *Chemical Modeling in Aqueous Systems II* (D.C. Melchior and R.L. Bassett, eds.), American Chemical Society Symposium Series 416, Chapter 31 pp. 398-413.

Rai, D. and Zachara, J.M. 1984. Chemical attenuation rates, coefficients, and constants in leachate migration. Volume 1: A critical review. Prepared by Batelle Pacific Northwest Laboratories. Electric Power Research Institute EA-3356. Vol 1.

Rai, D. 1987. Inorganic and organic constituents in fossil fuel combustion residues. Volume 1: A critical review. Prepared by Batelle Pacific Northwest Laboratories. Electric Power Research Institute EA-5176. Vol 1.