Using Synchrotron Radiation to Characterize Arsenical Smelting Products

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Outline

- Overview of Teck Cominco & Trail Ops
- Teck Cominco and synchrotron radiation
- Results of an As characterization study
  - #2 Baghouse Dust
  - Fe-As-Sb autoclave residue
- Potential applications
- Summary & Conclusions
Teck Cominco

- Canadian-based natural resource group
- Principal activities: mining, smelting, refining
- 2 Refineries
  - Trail, BC
  - Cajamarquilla, Peru
- Mines in Canada, USA and Peru
  (Zn, Pb, Cu, Mo, Au, coal)
Trail Operations

- Largest integrated Zn-Pb smelting & refining complex of its type in the world
- Capacities: 290,000 t/y Zn, 120,000 t/y Pb
- Ag, In, GeO$_2$, Bi, Cd, Au, low alpha Pb
- sulphuric acid, ammonium sulphate, SO$_2$, elemental S, copper arsenate, copper sulphate, sodium antimonate
- High level of environmental awareness
Teck Cominco & SR

- Teck Cominco & CLS members of CAMIRO
  - organization that promotes and manages collaborative research within mining industry

- CLS sponsored a demo project at APS for CAMIRO members (March 2002)
  - demonstrate the use of SR-based techniques to mining/metallurgical industry (As and Se)
  - option to attend demo and bring samples
XANES & XAFS

- X-ray absorption near edge structure
  - measures characteristic absorption of an X-ray with an electron in a particular core energy level
  - very sensitive to oxidation state
  - main absorption band for As: $4p \leftarrow 1s$

- X-ray absorption fine structure
  - interaction with neighbouring atoms
  - can “sit” on absorption band of an element and “look out” at local environment
Demonstration at APS

- Advanced Photon Source
  - Chicago, IL
  - PNC-CAT beamline
- Sent arsenic samples for analysis
- Samples compared to arsenic standards
  - AsFeS
  - As$_2$O$_3$
  - FeAsO$_4$·2H$_2$O
#2 Baghouse Dust

- Product from lead refining
- Very fine dust - 60% Sb & 15% As
- Feed to produce copper arsenate and sodium antimonate
- Historically assumed to be mixture of Sb$_2$O$_3$ and As$_2$O$_3$
- Actual speciation important for present and future processing options
SEM & XRD

- **SEM**
  - very fine As & Sb oxides (< 1µm)

- **XRD**
  - predominantly senarmontite (Sb$_2$O$_3$)
  - essentially “amorphous”
  - likely As$_2$O$_3$ (virtually identical to Sb$_2$O$_3$)
  - possibly As-O-Sb, but lines also identical
SR Results for #2BHD

- **XANES** (in a matter of seconds)
  - quantitatively As(III)

- **XAFS**
  - high degree of fine structure (“very crystalline”)
  - 1st NN is O (i.e. As-O)
  - 2nd NN is NOT As (i.e. not As-O-As)
  - due to high [Sb], As-O-Sb most likely
  - mostly Sb$_2$O$_3$ with some SbAsO$_3$
Fe-As-Sb Residue

- Research project to investigate options to stabilize arsenic and antimony for storage
- #2BHD autoclaved with $\text{Fe}_2(\text{SO}_4)_3$ to precipitate $\text{Fe}_x(\text{AsO}_4)_y$
- Residue: 55% Sb, 14% As, 17% Fe
  - SEM: identified Sb-Fe-As-O & Sb-As-Fe-O
  - XRD: possible $\text{As}_2\text{O}_3$
    - “unidentified phase with 3 broad peaks, poor crystallinity and possible hydroscopic nature”
SR Results for Residue

- **XANES**: 30% As$^{3+}$, 70% As$^{5+}$
- **XAFS**: does not match any standards
  - 1st NN is O (i.e. As-O)
    - As(V) as AsO$_4^{3-}$
    - As (III) as unreacted #2BHD
  - 2nd peak is split, so 2nd NN is ...
    - Fe(?) - but not scorodite or amorphous FeAsO$_4$
      - possibly AsO$_4^{3-}$ adsorbed on ferrihydrite
    - Sb(?) - matches 2nd peak of #2BHD
      - 30% unreacted starting material (#2BHD)
Fourier Transform of XAFS

As$^{5+}$ is As-O (i.e. AsO$_4^{3-}$)

AsO$_4^{3-}$ adsorbed on ferrihydrite

As-O-Sb (#2BHD)
Summary

- #2BHD
  - As present is quantitatively trivalent
  - As$^{3+}$- O in #2BDH is NOT As$_2$O$_3$
  - Sb$_2$O$_3$ with AsSbO$_3$ (As-O-Sb)
- Fe-As-Sb Residue
  - ~ 30% As not completely oxidized
  - As$^{5+}$ is AsO$_4^{3-}$, possibly adsorbed on ferrihydrite
  - also As-O-Sb, from unreacted starting material
Other applications ...

- Speciation & association of metals in ...
  - ores & concentrates (PGMs, Ag, Au, In, Ge)
  - mill tailings, effluents & other in-process materials
  - ARD
  - soils & sediments

- Speciation of surface coatings on minerals from various portions of flotation circuits

- Map slices of rock/ore/agglomerate

- Surface analysis to look for corrosion, cracks, layered coatings with high resolution
Conclusions

- SR-based techniques **valuable tools** for mining & metallurgical applications:
  - determine oxidation states
  - determine nearest neighbour associations
- Allows for characterization of material not possible by traditional methods
  - high resolution
- 2 additional projects ongoing with CLS
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Questions ?