Using Chromium Reducible Sulfur for AMD Prediction

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Standard AMD Prediction in Hard Rock Mining

- Assessment based on Acid Base Accounting and determination of sulfide sulfur content which can oxidise to produce acid.
- Since 2002 TOS (total oxidisable sulfur) is preferred method (AMIRA, DITR 2007, GARD Guide 2009).
- If TOS is >0.3 % then acid neutralisation capacity (ANC) is tested to calculate the theoretical Net Acid Production Potential (NAPP). Net Acid Generation (NAG) by oxidation and NAG pH is also tested.

Sulfur Form	Examples	Acid Formation Potential
Alkali and alkaline earth sulfate salts	Gypsum ($CaSO_4.2H_2O$) Epsomite ($MgSO_4.7H_2O$) Barite ($BaSO_4$)	Nil
Iron and aluminium sulfates	Jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$) Alunite ($KAl_3(OH)_6(SO_4)_2$)	Produces some acid by hydrolysis
Thiosulfates, sulfites, polythionates	Thiosulfate ($S_2O_3^{2-}$) Dithionate ($S_2O_6^{2-}$)	Produces some acid by oxidation
Elemental sulfur	Sulfur (S)	Produces 30.6 kg H_2SO_4 /tonne by bacterial oxidation
Iron sulfides	Pyrite (FeS_2) Marcasite (FeS_2)	Produce 30.6 kg H_2SO_4/tonne by oxidation
	Pyrrhotite ($Fe_{(1-x)}S$)	Produces <30.6 kg H_2SO_4/tonne by oxidation, depending on oxygen supply.
Mixed iron-base metal sulfides	Chalcopyrite (CuFeAs2) Pentlandite ($(Fe,Ni)_9S_8$) Bornite (Cu_5FeS_4)	Produces <30.6 kg H_2SO_4/tonne by oxidation, depending on iron to base metal ratio
Base metal sulfides	Chalcocite (Cu_2S) Covellite (CuS) Galena (PbS) Sphalerite (ZnS)	Do not produce acid by oxidation
Arsenic and molybdenum sulfides	Arsenopyrite (FeAsS) Realgar (As_4S_4) Molybdenite (MoS_2) Orpiment (As_2S_3)	May produce >30.6 kg H_2SO_4/tonne by oxidation

Chromium Reducible Sulfur (CRS)

Designed For:

- Coal Mines
- Acid Sulfate Soils (main use in WA)

In Which:

- Sulfides present exclusively as pyrite or marcasite, are normally fine grained and highly reactive
- Often high organic content and organic sulfur present – CRS avoids this interference
- CRS is a direct measure of sulfide sulfur – cheaper than TOS

Can it be used for hard rock mining?
Only one previous paper with validation for some minerals other than pyrite.

Laboratory Study of TOS Versus CRS for AMD

- Total of 54 samples of waste rock and tailings, some pure minerals
- Gold, iron ore, copper, nickel and lead/zinc mines
- TOS, CRS, ANC, NAG, NAG pH, XRD, Total Metals
- Range of Sulfide Minerals including:
  - Iron Sulfides (pyrite, pyrrhotite and marcasite)
  - Chalcopyrite ($CuFeS_2$) and Chalcocite (Cu_2S)
  - Arsenopyrite ($FeAsS$)
  - Stibnite (Sb_2S_3)
  - Galena (PbS)
  - Sphalerite (ZnS)
  - Pentlandite $(Fe, Ni)_9S_8$
  - Molybdenite (MoS_2)

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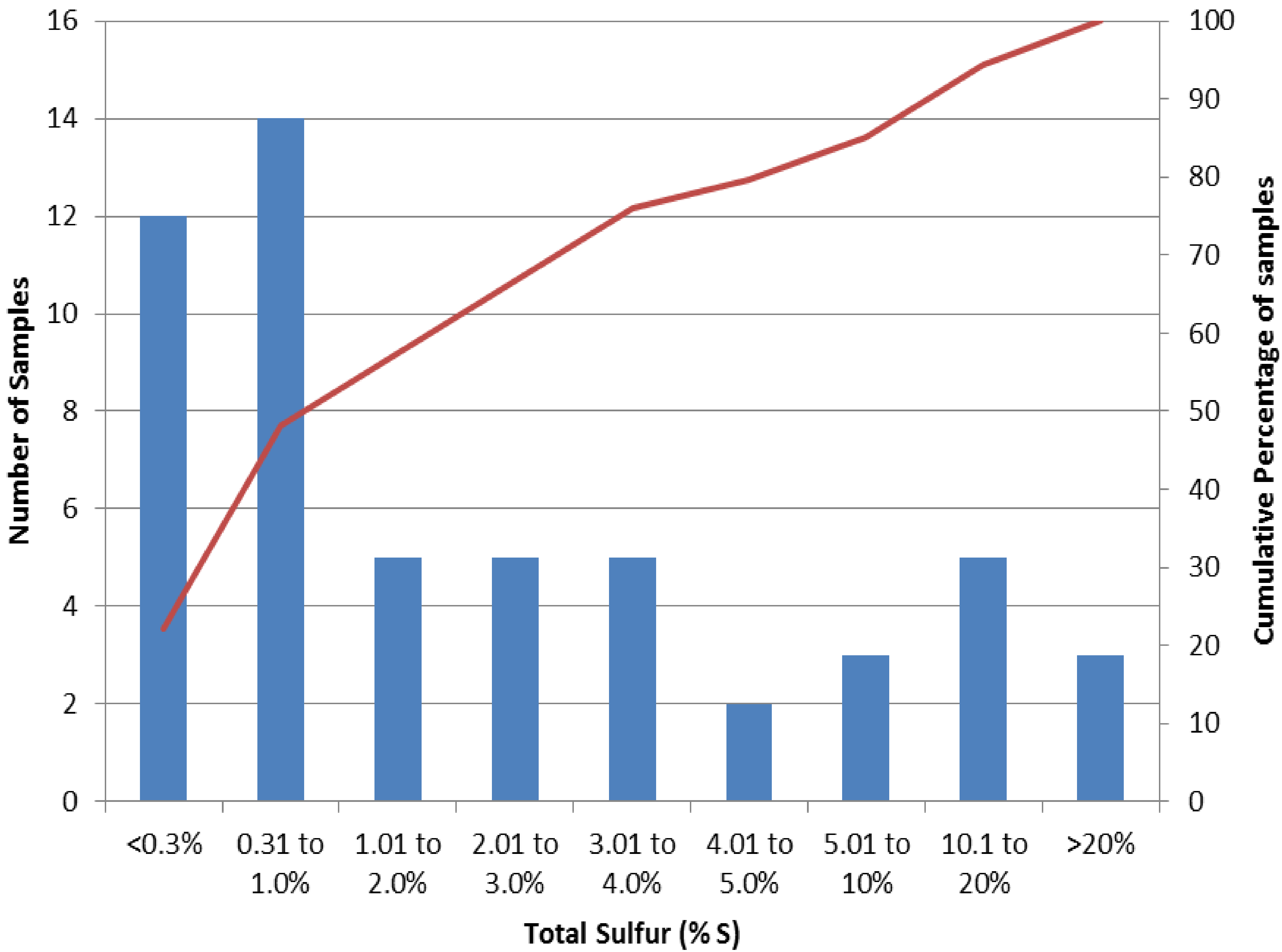

Number of Samples
Cumulative Percentage of samples
Total Sulfur (% S)
16
14
12
10
8
6
4
2
0
100
90
80
70
60
50
40
30
20
10
0
<0.3%
0.31 to 1.0%
1.01 to 2.0%
2.01 to 3.0%
3.01 to 4.0%
4.01 to 5.0%
5.01 to 10%
10.1 to 20%
>20%

Traditional AMIRA TOS Classifications

- 9 Samples ‘Barren’ – mostly Iron Ore Waste
- 13 Samples non acid forming (NAF)
- 28 Samples potentially acid forming (PAF)
- 4 Samples ‘Uncertain’ - acid predicted was not generated:
    - One iron ore waste sample (interference of insoluble barite or celestite?)
    - Two lead/zinc mine waste samples (galena/sphalerite are not acid producing)
    - One sample of pure chalcocite (did not generate acid under lab conditions)

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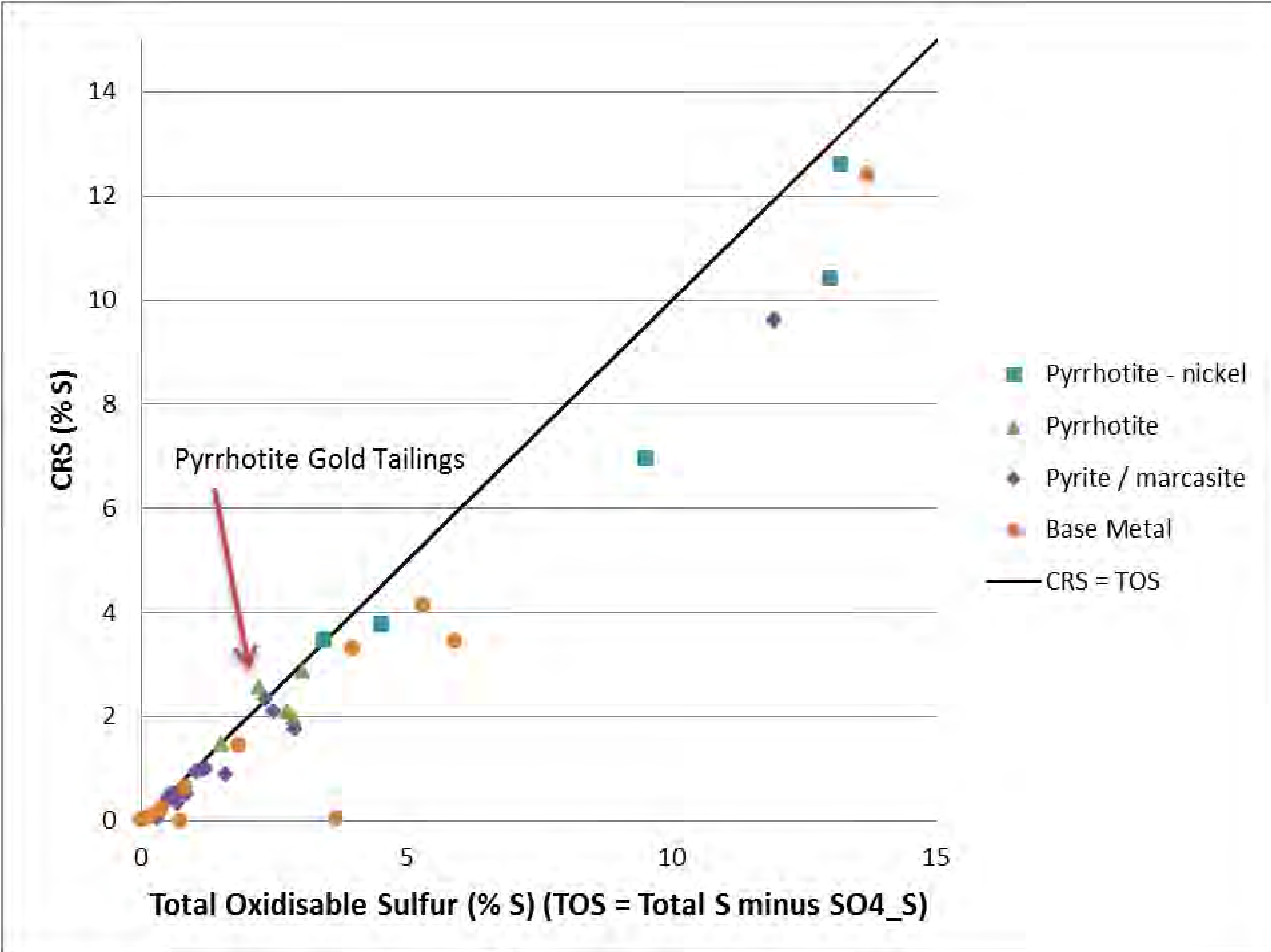
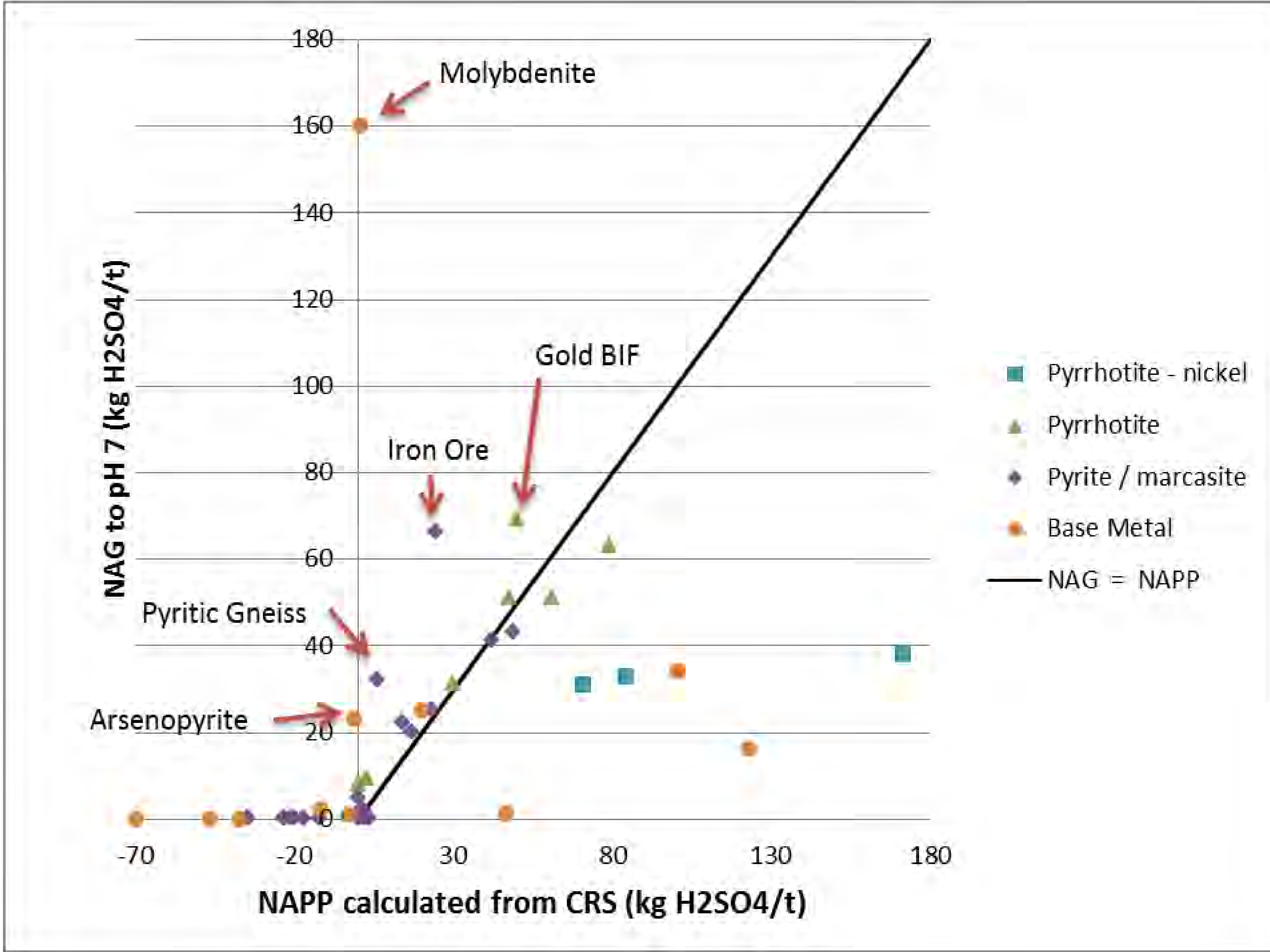


14
12
10
8
6
4
2
0
CRS (% S)
0
5
10
15
Total Oxidisable Sulfur (% S) (TOS = Total S minus SO4_S)
Pyrrhotite Gold Tailings
Pyrrhotite - nickel
Pyrrhotite
Pyrite / marcasite
Base Metal
CRS = TOS

Predicted NAPP (CRS or TOS) Versus NAG

- NAG from gold waste samples closely matched values from TOS. CRS prediction also matched overall but was more variable.
- Only molybdenite was underestimated by TOS. CRS grossly underestimated acidity for molybdenite.
- Neither TOS or CRS correctly predicts Ni, Cu, Pb and Zn sulfides – the ABA factor of 30.6 times sulfide content based on pyrite does not fit these metals.



Molybdenite
Gold BIF
Iron Ore
Pyritic Gneiss
Arsenopyrite
180
160
140
120
100
80
60
40
20
0
-70
-20
30
80
130
180
NAG to pH 7 (kg H2SO4/t)
NAPP calculated from CRS (kg H2SO4/t)
Pyrrhotite - nickel
Pyrrhotite
Pyrite / marcasite
Base Metal
NAG = NAPP

Comparison of AMD Classification CRS Vs TOS

- Of the 54 samples - despite variation only 4 were classified differently:

  - Iron ore waste sample Uncertain by TOS and Barren by CRS. TOS interference from insoluble sulfate as barite or celestite?

  - Gold mine waste containing pyrrhotite was PAF based on TOS but Uncertain by CRS due to a much lower CRS (0.46%) versus TOS (0.62%). The NAG pH was 3.0 i.e. suspect PAF

  - Arsenopyrite and Molybdenite - both PAF by AMIRA/TOS and Uncertain by CRS

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Laboratory Variation in CRS Analysis

- Not ideal – Intra-lab variation Lab A 46% (5 reps) Lab B 8.8% (7 reps)
- Much worse - Laboratory B results were lower except for one sample of 44 repeated and average 40% lower for 1 to 10% CRS

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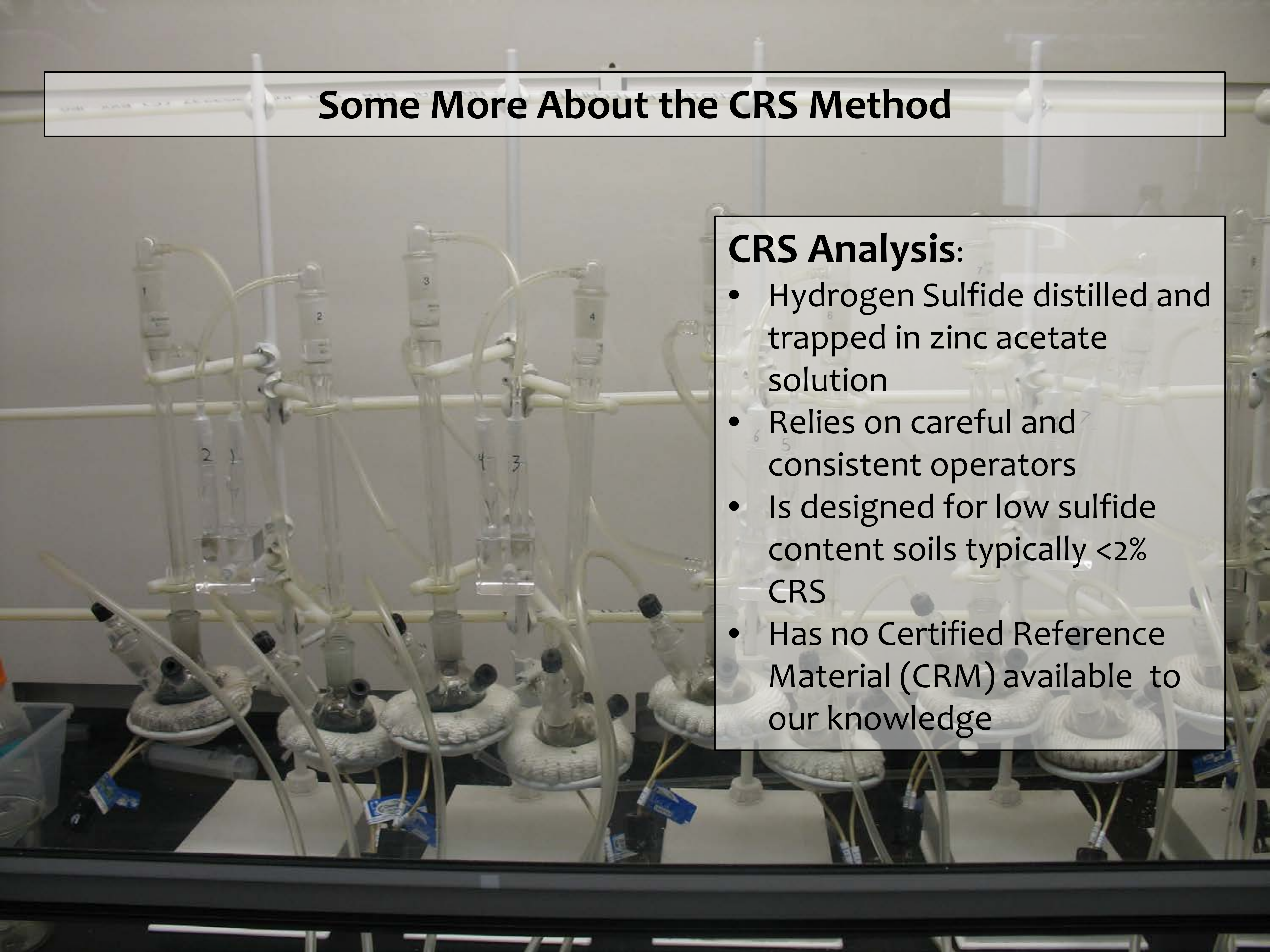
Some More About the CRS Method



CRS Analysis:

- Hydrogen Sulfide distilled and trapped in zinc acetate solution
- Relies on careful and consistent operators
- Is designed for low sulfide content soils typically <2% CRS
- Has no Certified Reference Material (CRM) available to our knowledge

Conclusions

- General agreement - TOS more conservative & less variable for AMD prediction.
- Bias for TOS is positive (high) & CRS is mostly negative (low).
- Of 54 samples, five resulted in significantly more acid production than CRS predicted (none for TOS) – two were arsenopyrite and molybdenite which gave no recovery by CRS. Large pyrite crystals (versus soils) a factor?
- Significant issues with inter-lab results for CRS – method modifications and a CRM are needed for hard rock samples.
- CRS does have good potential with more work on lab issues for iron ore waste (typically low sulfides, insoluble sulfates which affect TOS).
- Neither method works for Pb/Zn sulfides – ABA gives false classification as acid forming. Cu/Ni sulfides need mineralogy, ABA overestimates acid.

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Study funded by CRC CARE, conducted by MBS and ChemCentre -QUESTIONS?

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