The Basics of Self-heating of Sulphide Mineral Mixtures©

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Self-heating or *Spontaneous heating*

- Self induced **temperature rise** due to accumulated heat resulting from internal exothermic reactions
- Under favourable conditions the temperature of the material can be raised to the point of **auto-ignition** or **spontaneous combustion** i.e. burning
- Not to be equated to **pyrophoric behaviour** which refers specifically to auto ignition (in air) <55^{o}C

Presentation will address

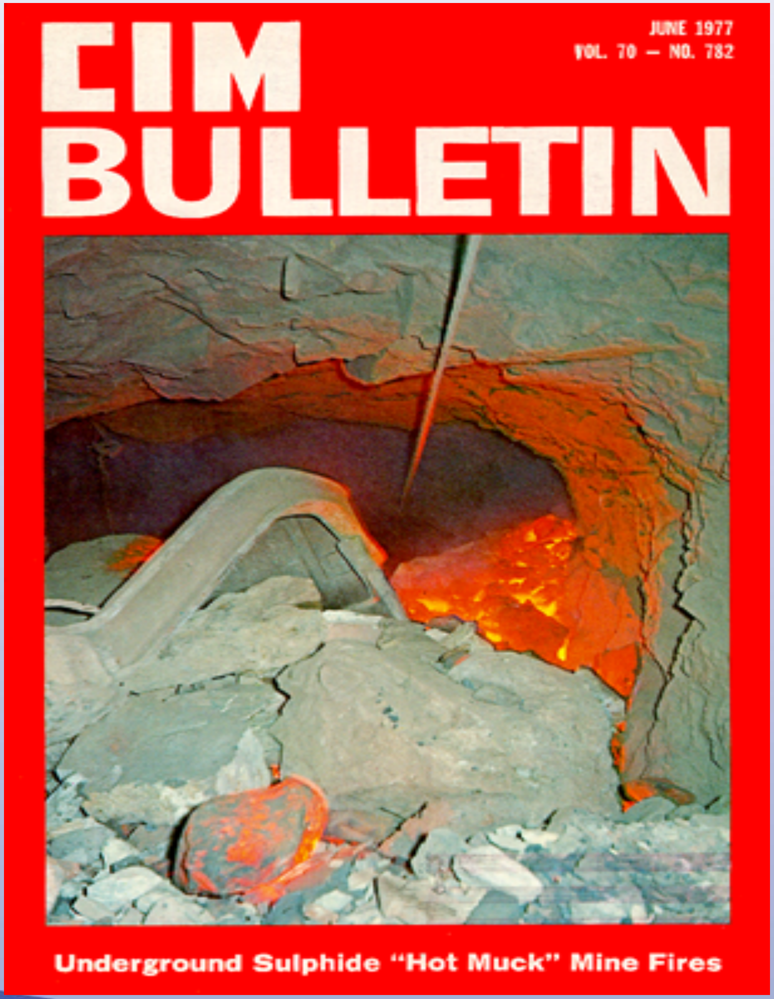
Part 1: Basics of Sulphide Self-Heating

- Stages of heating
- The FR-2 test
- Chemical equations
- Role of mineralogy
- Key variables

Part 2: Field Examples & Mitigation Strategies

Examples of Self-Heating in the mining industry

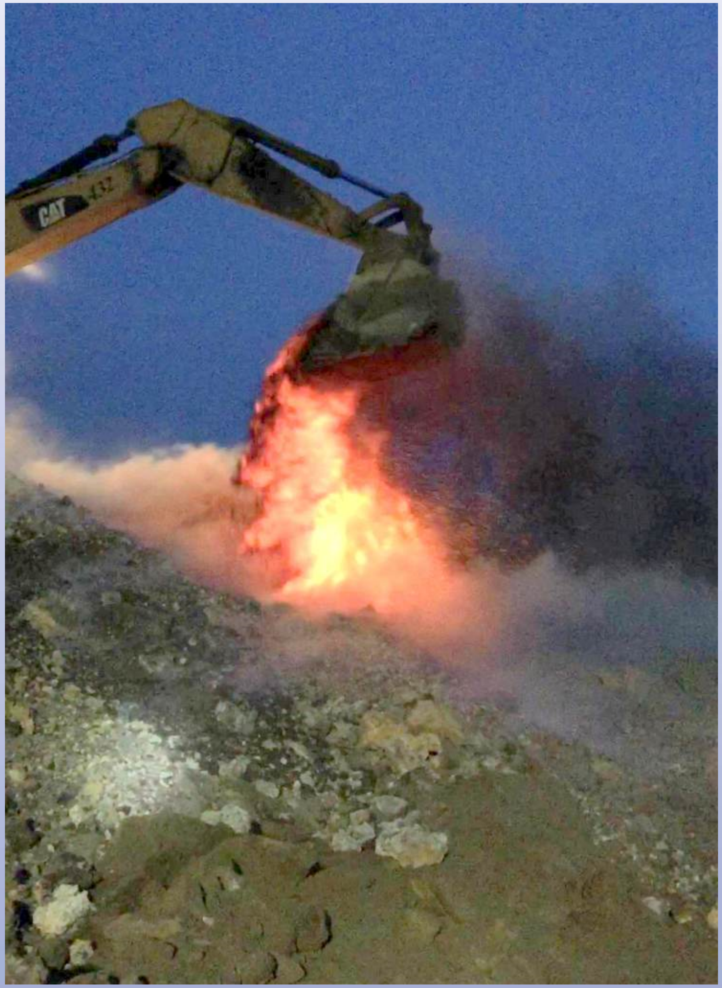
Underground (high Po ore) -Sullivan Mine (British Columbia)



First mentioned as an issue at the Sullivan mine in 1926 CIM Magazine article (O'Brien and Banks)

CIM Bulletin, June 1977, Farnsworth

Surface Stockpile (Ni sulphide ore)



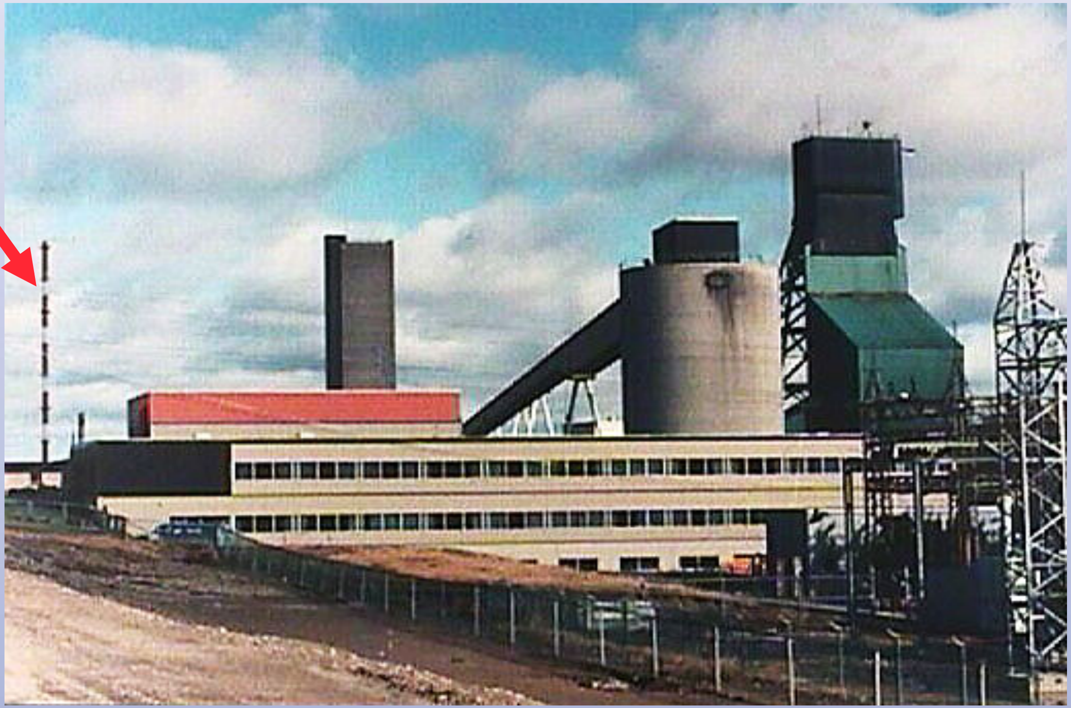
Reactive pentlandite pyrrhotite ore

Reached roasting temperatures in hours (>350 ^{o}C)

Underground: waste rock fill -high pyrrhotite content

Brunswick Mine

SO_2 Venting Stack



Fire burned for over 25 years in sealed-off stopes

Underground: Broken Paste Fill fires at Louvicourt and Brunswick

Louvicourt: L to R
Unreacted fresh paste
Partly oxidized (~2-300 ^{o}C)
Fully oxidized (~400^{o}C)
(Bernier and Li, 2003)

Brunswick oxidized paste

- Blasting of stopes caused breakage of adjacent paste-filled areas
- Broken paste began heating and releasing SO_2
- Mitigation strategy was to keep pyrrhotite < 10%

Open Pit: Deflagration in Loaded Blast Holes – Red Dog Pb/Zn mine

- Interactions of reactive sulphide rock cuttings with blasting agents in loaded blast holes
- Deflagration event began 6-7 hrs after loading, lasted ~2 hrs

Courtesy of N. Paley;
Teck Minerals' Red Dog mine

Sulphide Waste Rock Dump
Pb-Zn ore

Trench dug to expose burning waste rock

Oxidized lumps of waste rock

SO_2 and steam evolution

Tailings Berms
Pb-Zn ore

"sintered" lumps of tailings

SO_2 and steam evolution

Evidence of layer of oxidation and elemental sulphur at distance below surface

Concentrate Storage Piles at Port sites

Cu Conc
Measured
150 ^{O}C and
16 ppm SO_2

Zn Conc
Fire at
storage silo

"hot spot" in
Ni conc pile

Concentrate Fire in Ship's Hold

Zinc sulphide concentrate

Related Issues

Mine and Mill Safety: SO_2 gas, noxious vapours, increased temperatures, reduced oxygen content, “frozen” ore passes, damaged infrastructure

Environmental: Air and water contamination

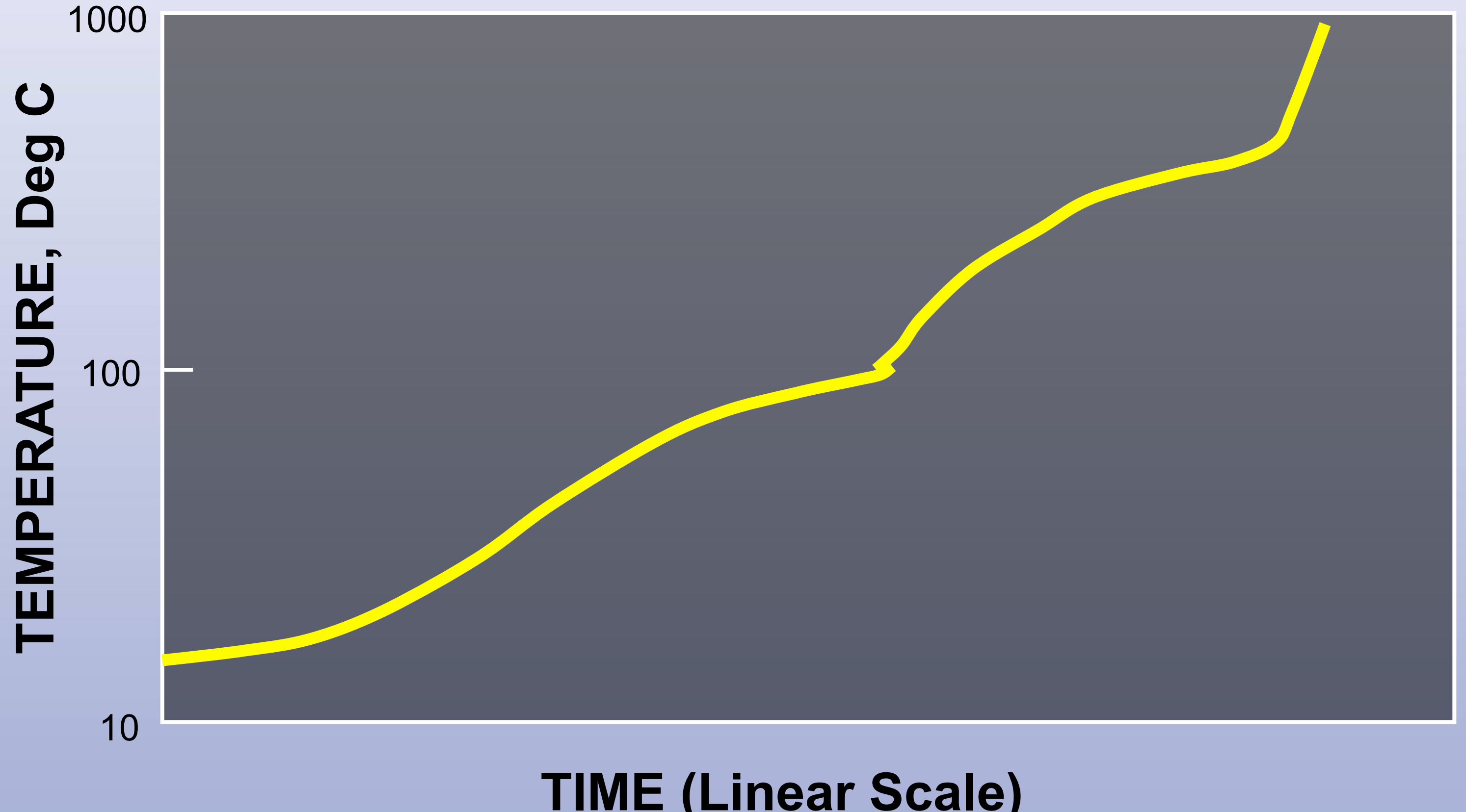
Transportation: Fires in storage sheds and vessels (ships, rail cars, containers)

Metallurgical Performance: Decreased recovery due to sulphide mineral oxidation

Metallurgical Accounting: Weight gain and metal assay decrease in concentrate

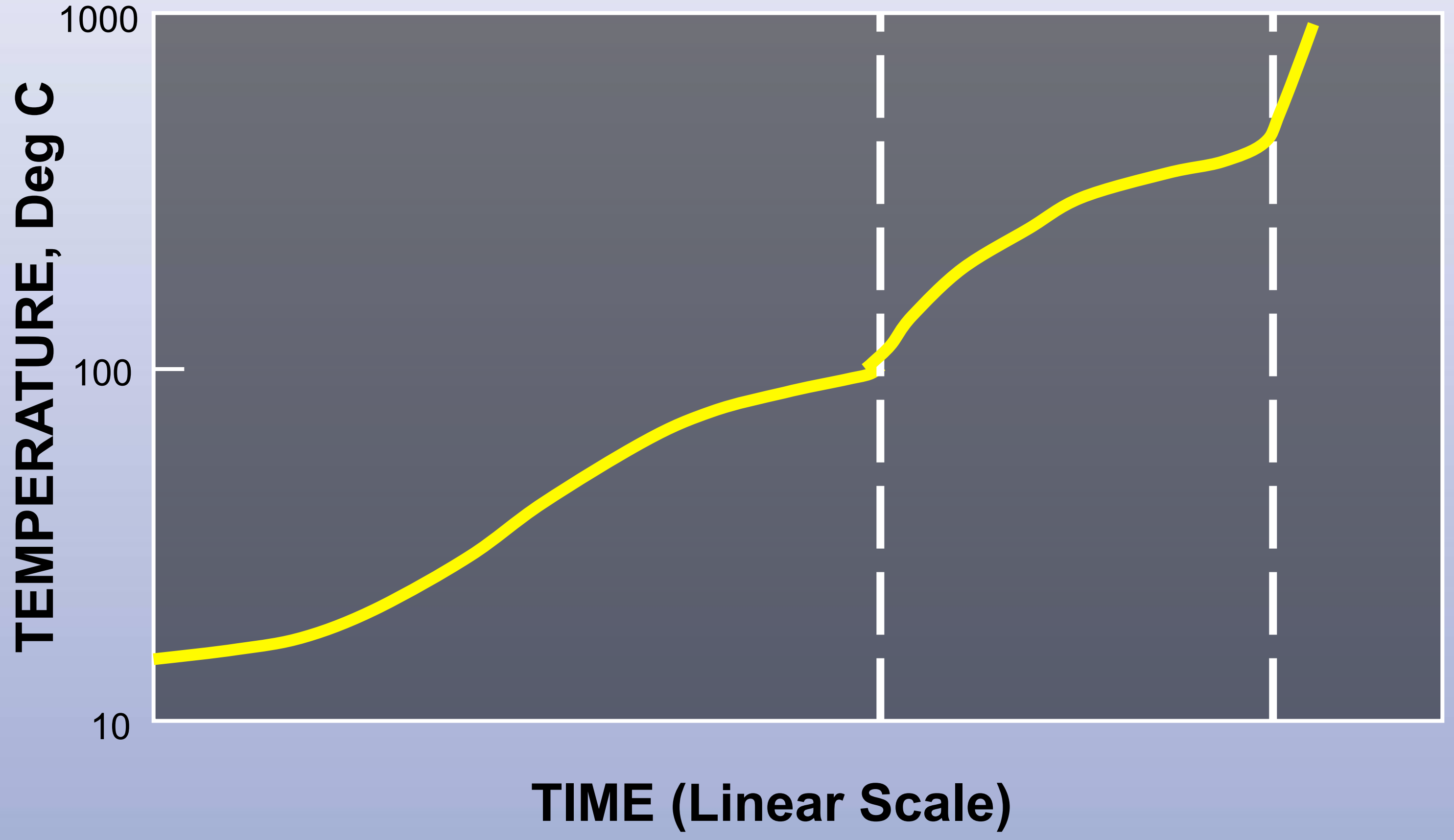
Characterizing Self-heating Behaviour: What is observed

Temperature rise versus time for sulphide mixture heating

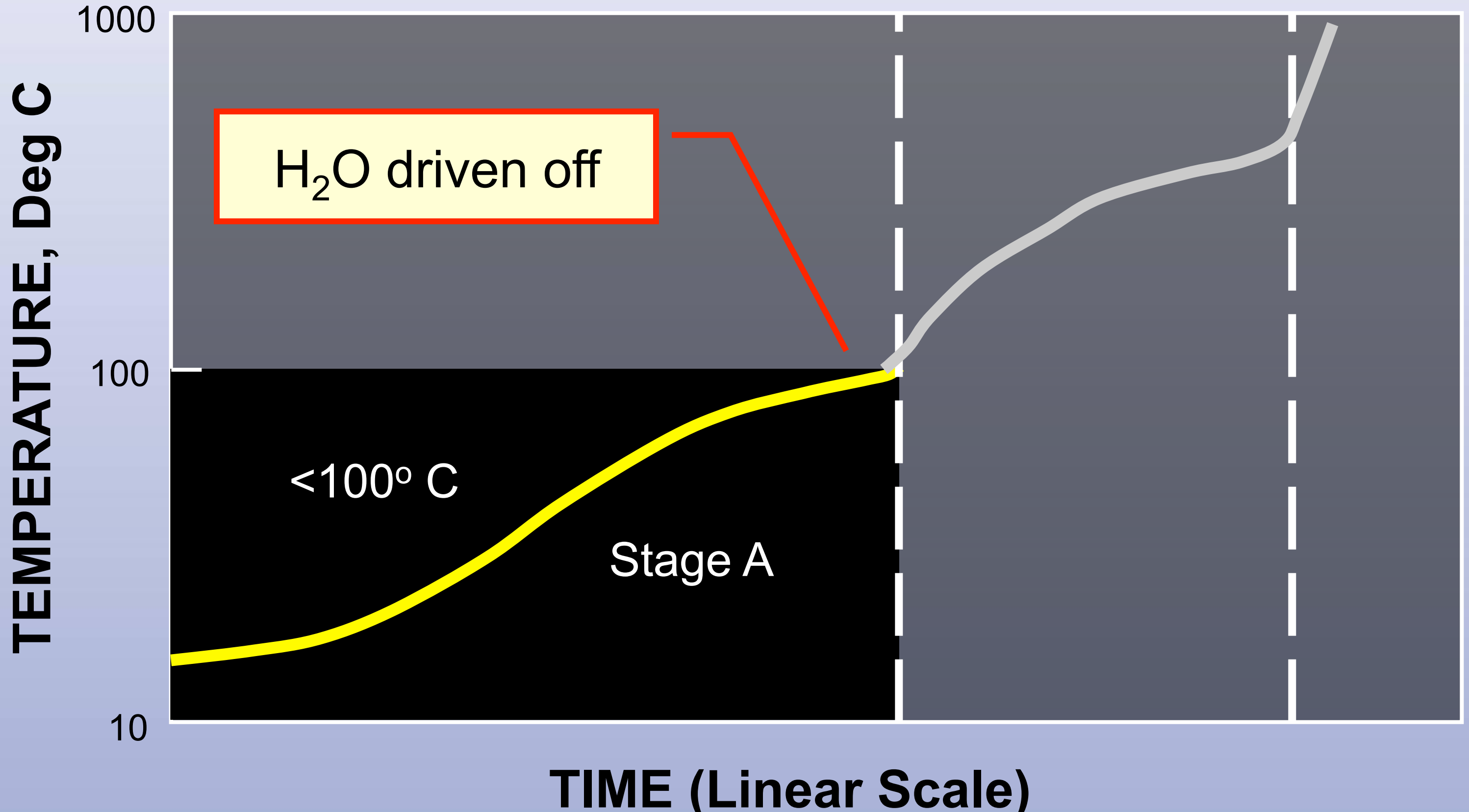


Rosenblum and Spira, 1981

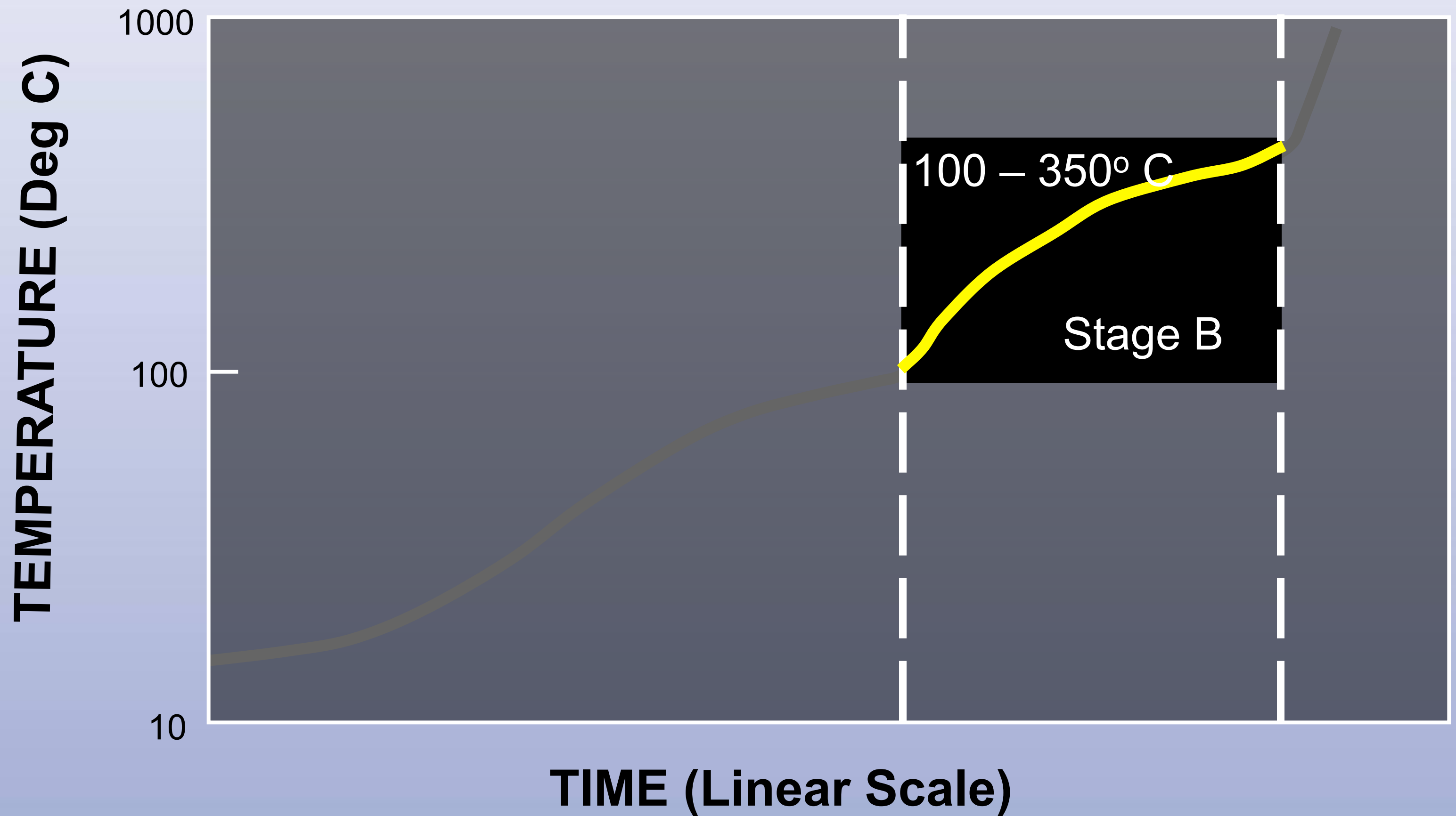
Schematic Representation of Temperature Rise – 3 Regions



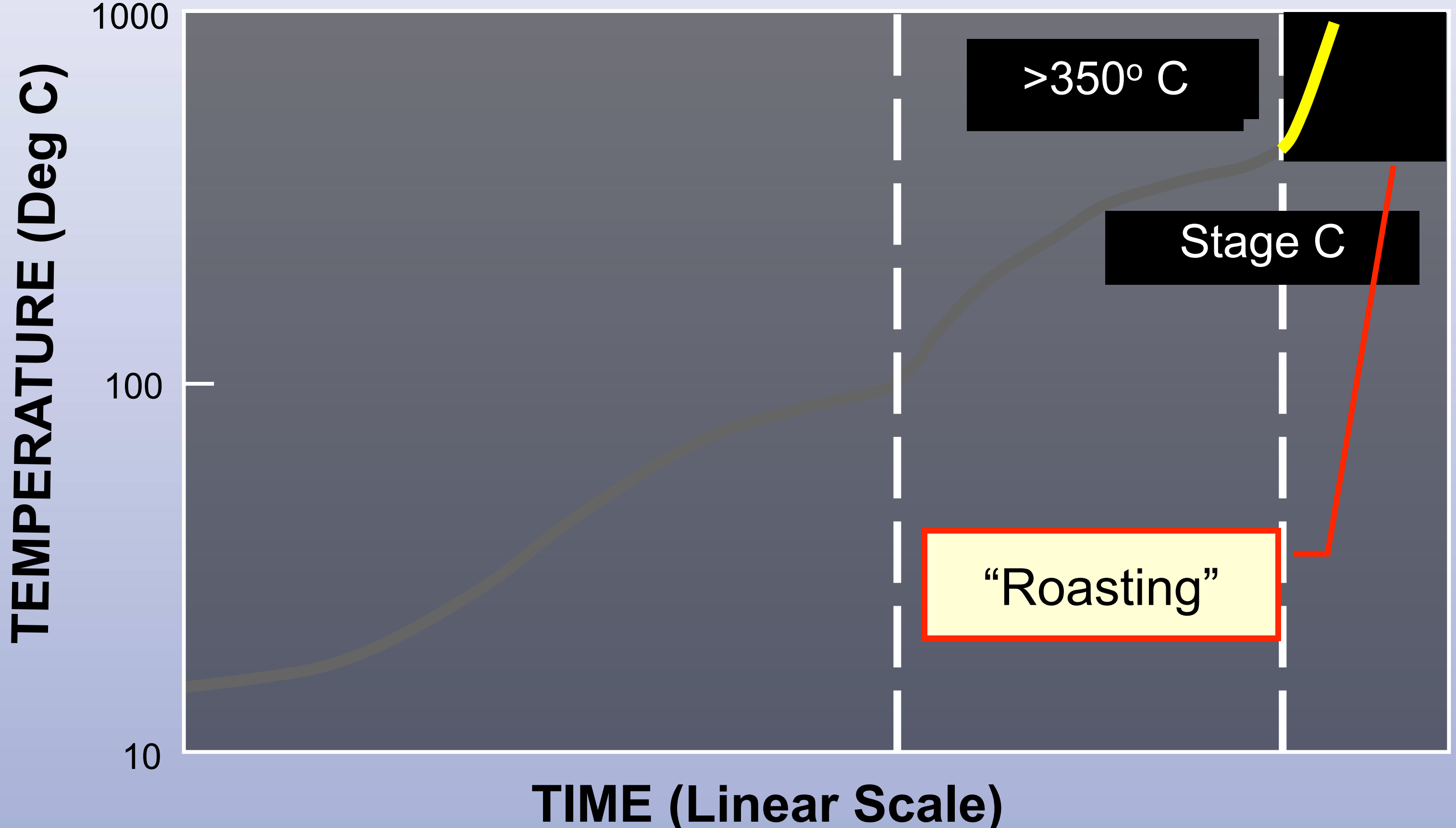
Schematic Representation of Temperature Rise – Stage A



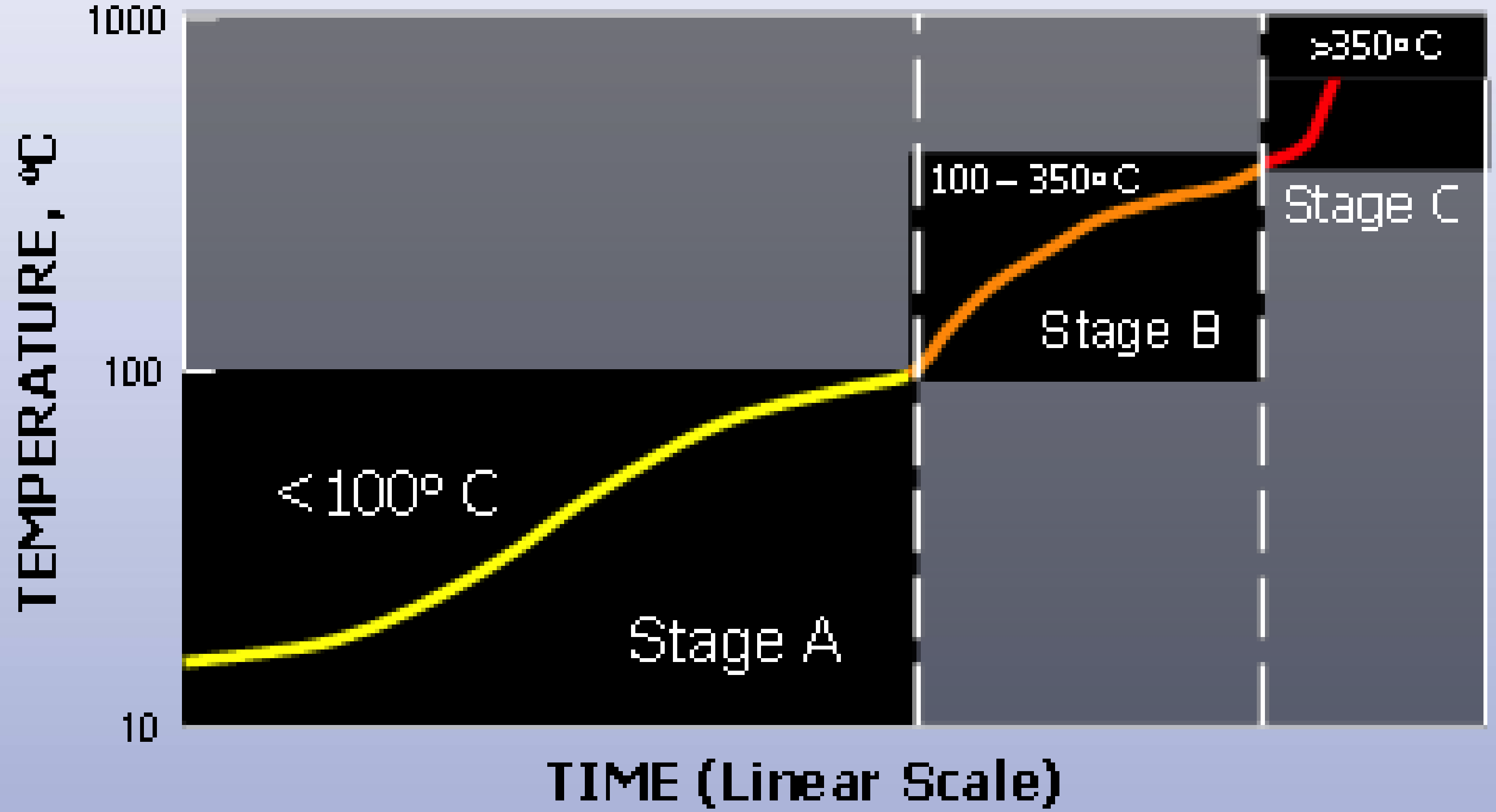
Schematic Representation of Temperature Rise – Stage B



Schematic Representation of Temperature Rise – Stage C



Schematic Representation of Temperature Rise – Overall

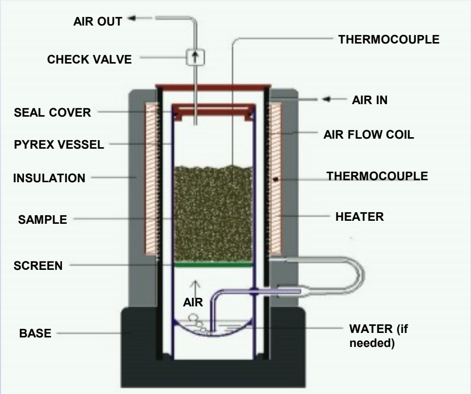


How do we quantify the potential to self-heat?

Standard Stage A and B (FR-2Test) SH test conditions: 500 g sample

Stage A
- 6% moisture
- 70 ^oC
- 48 hrs

An accelerated "weathering" stage



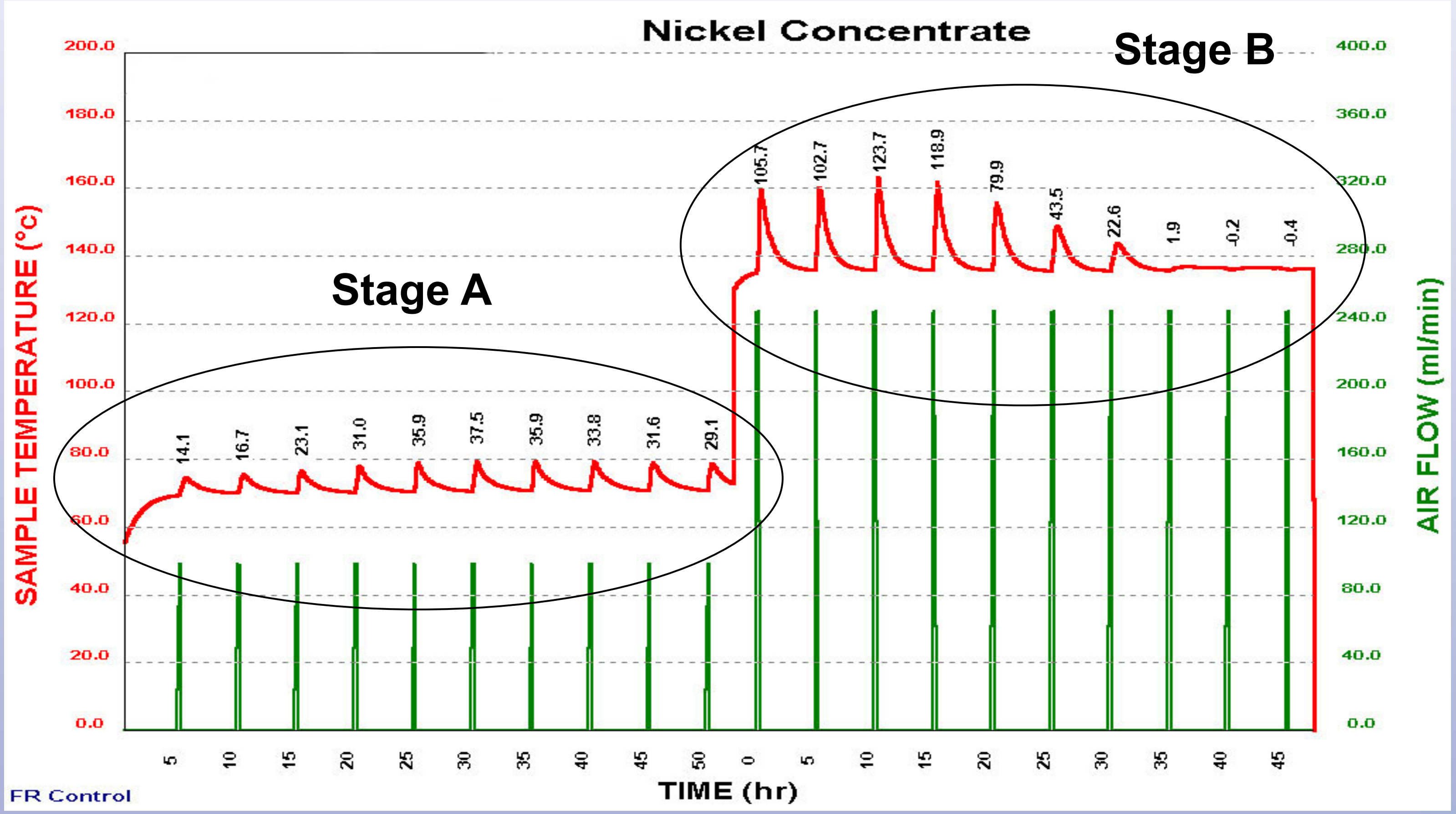
The FR-2 Apparatus

Stage B
- Continues from Stage A
- 140 ^oC
- 48 hrs

Oxidation at elevated temperature (moisture driven off)

Air is blown in for 15 min every 5 hours

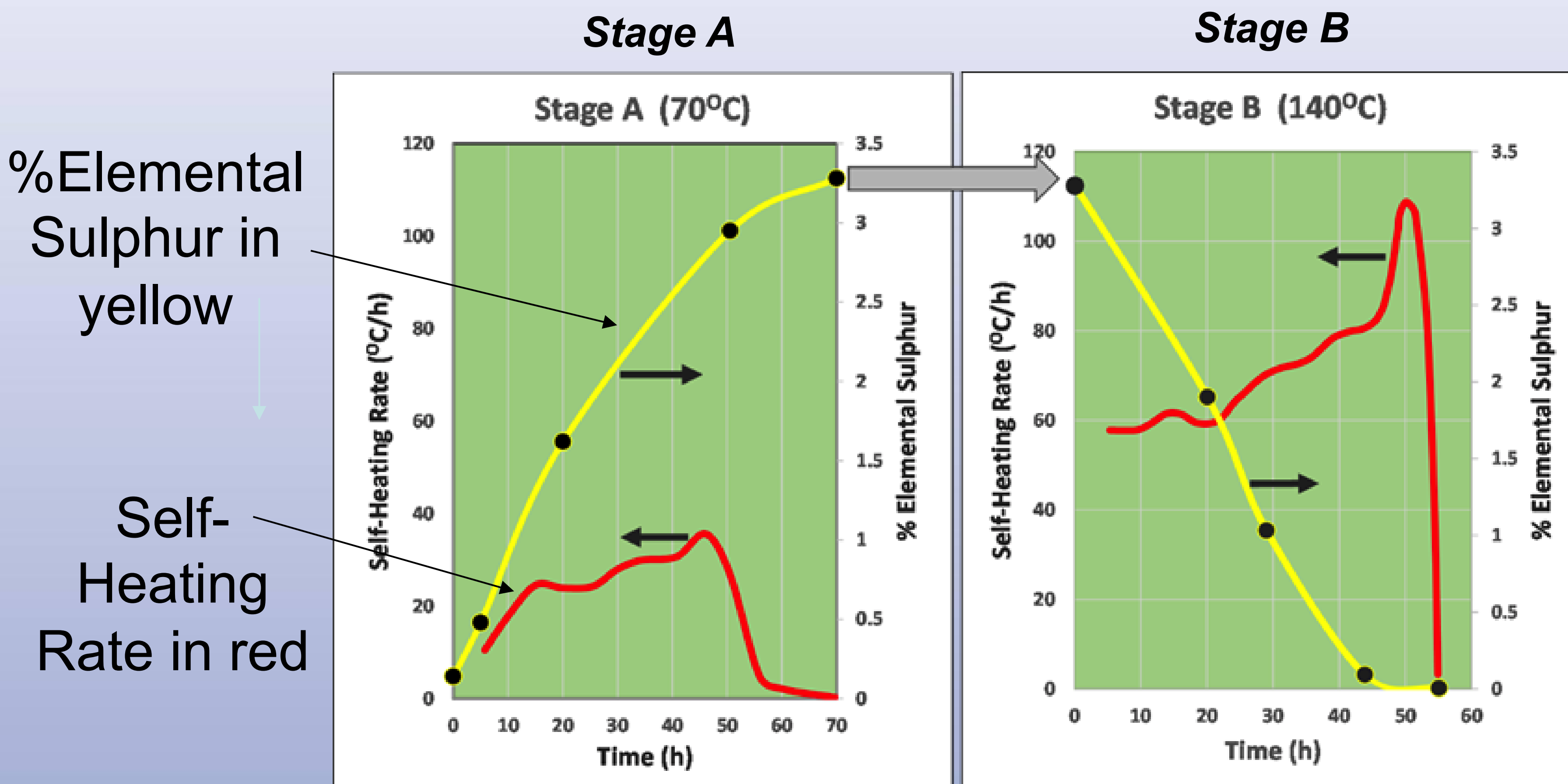
Example Results
- the SH Thermogram



The Key Role of Elemental Sulphur

Key Understanding

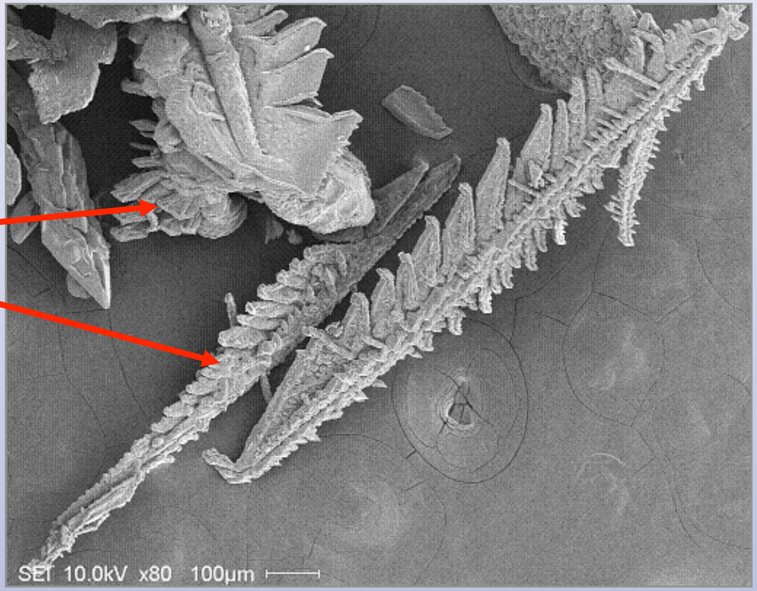
Elemental Sulphur Formed in Stage A is Oxidized to SO_2 in Stage B



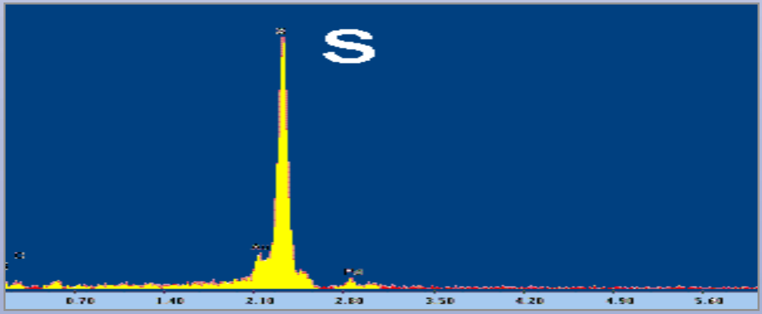
Sulphide rich tailings

SEM Image of Elemental Sulphur Formed in Stage A

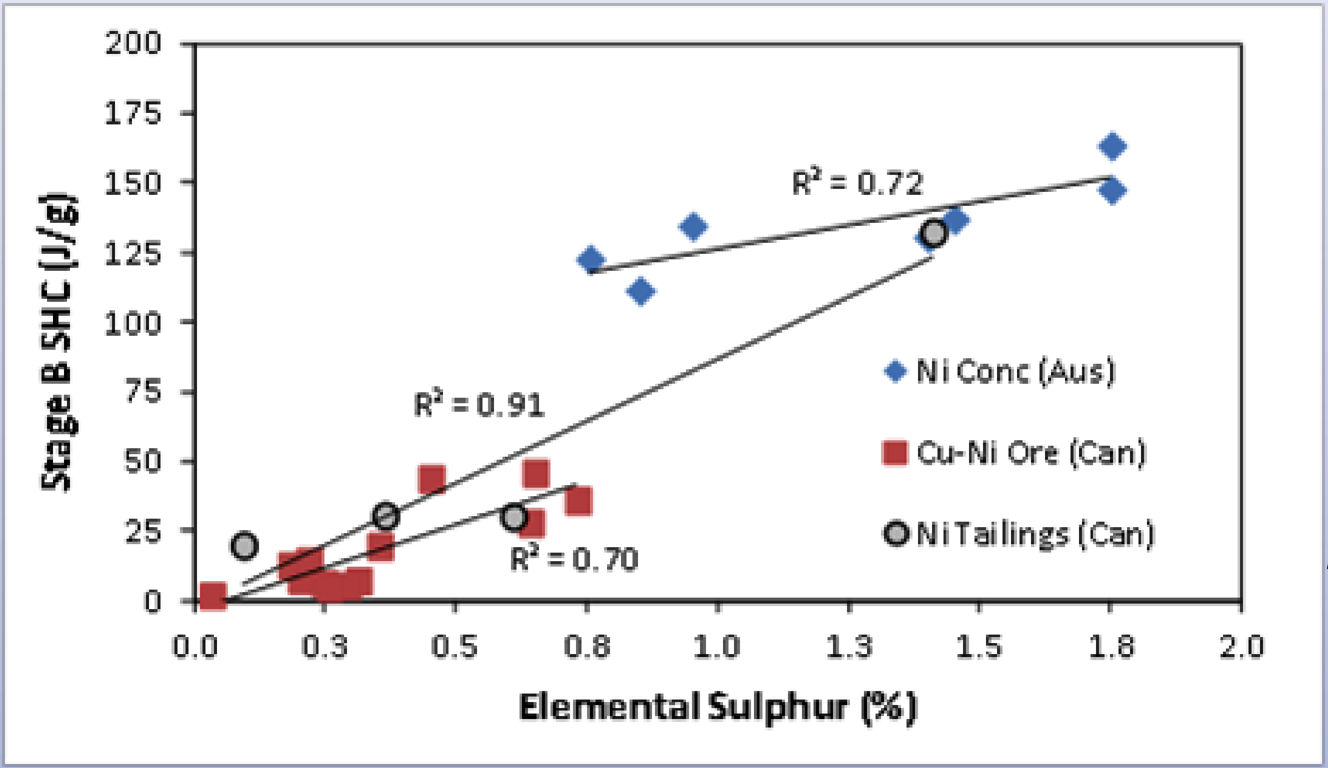
Elemental sulphur precipitates



Note: Simply adding sulphur to inert material does not result in self-heating



Stage B Heating is Proportional to the Amount of Elemental Sulphur Formed



Elemental sulphur often evident in the field

Data is for ores, concentrates and tailings

What is Going On?

Basic Chemical Reactions

Postulated reaction sequence

1. Initial oxidation or "weathering" of sulphide minerals will result in some acid formation

$$Fe_{1-x}S + (2 - 1/2\,x)O_2 + xH_2O = (1-x)Fe^{2+} + 2xH^+ + SO_4^{2-}$$

2. The acidity and sulphide will result in H_2S formation

$$Fe_{(1\text{-}x)}S + 2H^+ = H_2S + (1\text{-}x)Fe^{2+} \text{ (see note)}$$

Stage A

3. Under reduced O_2 pressure S° is preferentially formed from H_2S (other SO_x products also formed)*

$$2(H_2S)_g + (O_2)_g \rightarrow 2\alpha S^\circ + 2(H_2O)_{aq} + \underline{HEAT}$$

4. S° is oxidized to SO_2 +<u>HEAT</u>

$$\beta S^\circ + (O_2)_g \rightarrow SO_2 + \underline{HEAT}$$

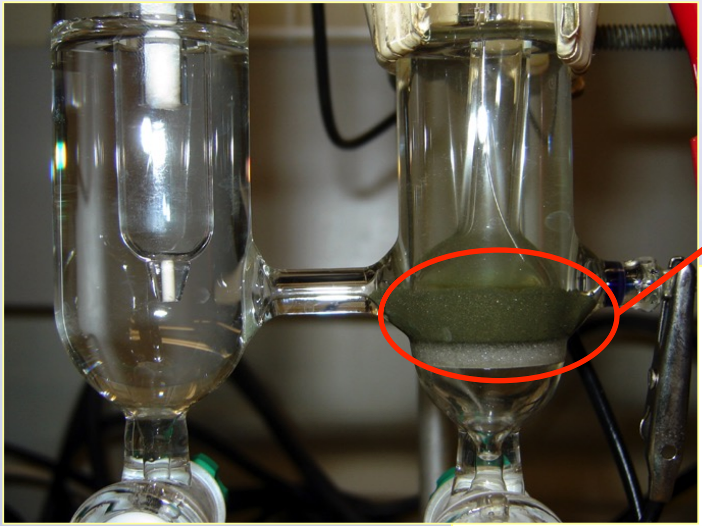
Stage B

*Note: Alternate, $S_2^{2-} + 2Fe^{2+} + 2H^+ \rightarrow H_2S + S^{2-} + 2Fe^{3+}$ and $Fe^{3+} + e \rightarrow Fe^{2+}$

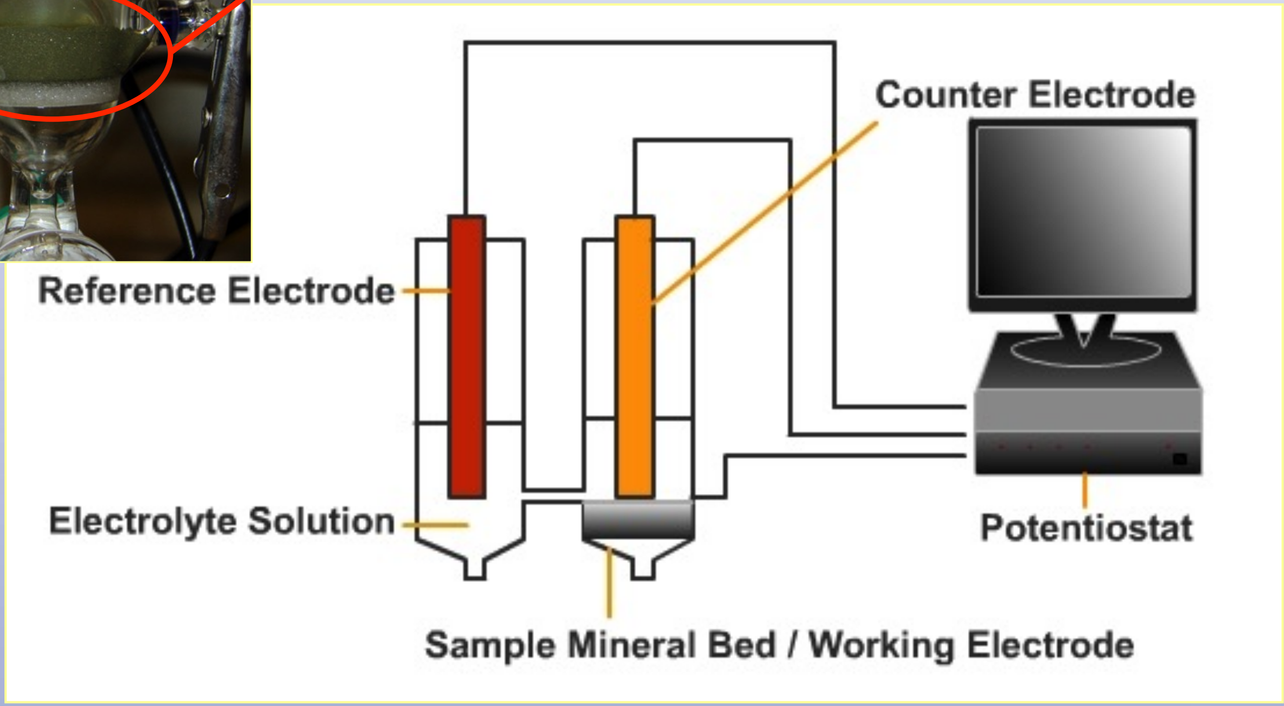
What is Going On?

We Need a Mixture of Sulphides (electrochemical reactions)

Measurement of mineral rest potential, E_M With potentiostat



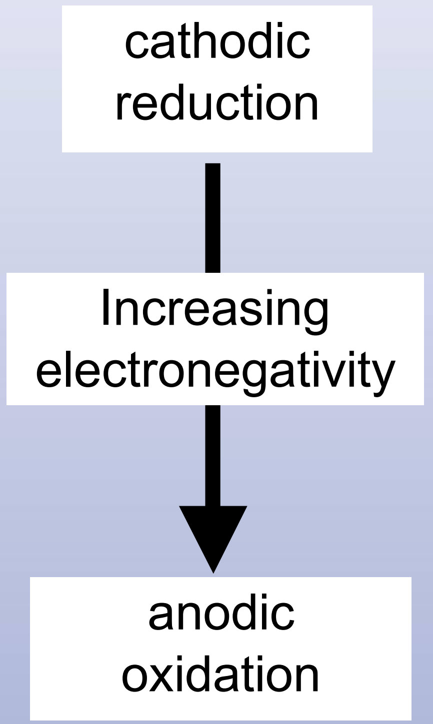
mineral bed electrode



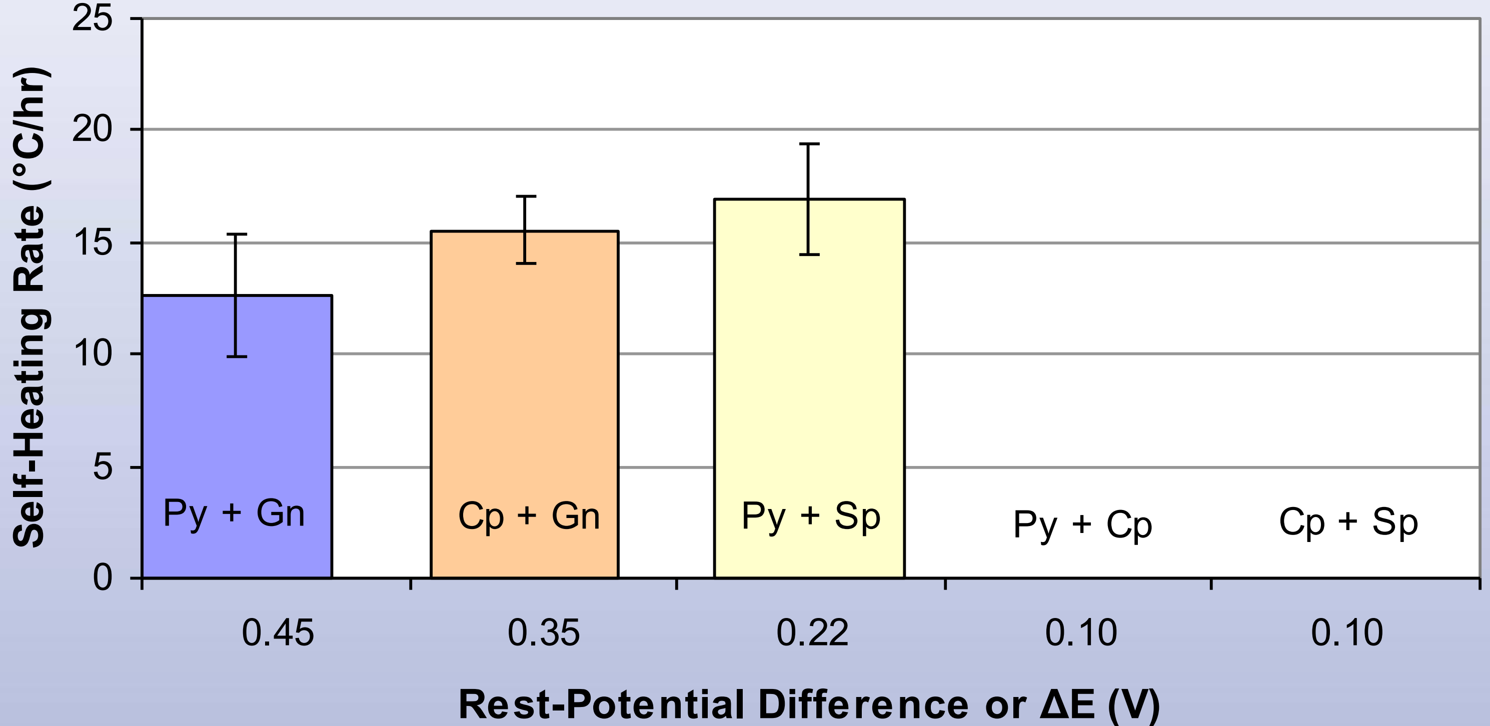
E_m values are a function of pH

Results – Rest Potential Individual sulphides (pH 7)

Mineral		Rest Potential vs SHE *volts*
Pyrite	FeS_2	0.66
Marcasite	FeS_2	0.63
Chalcopyrite	$CuFeS_2$	0.56
Sphalerite	ZnS	0.46 to -0.24
Covelite	CuS	0.42
Bornite	Cu_5FeS_4	0.4
Pyrrhotite	$Fe_{(1-x)}S$	0.31 to -0.28
Chalcocite	Cu_2S	0.44 to 0.31
Galena	PbS	0.28
Molybdenite	MoS_2	0.11



Results for Mineral Mixtures Stage A SHR (°C/hr)

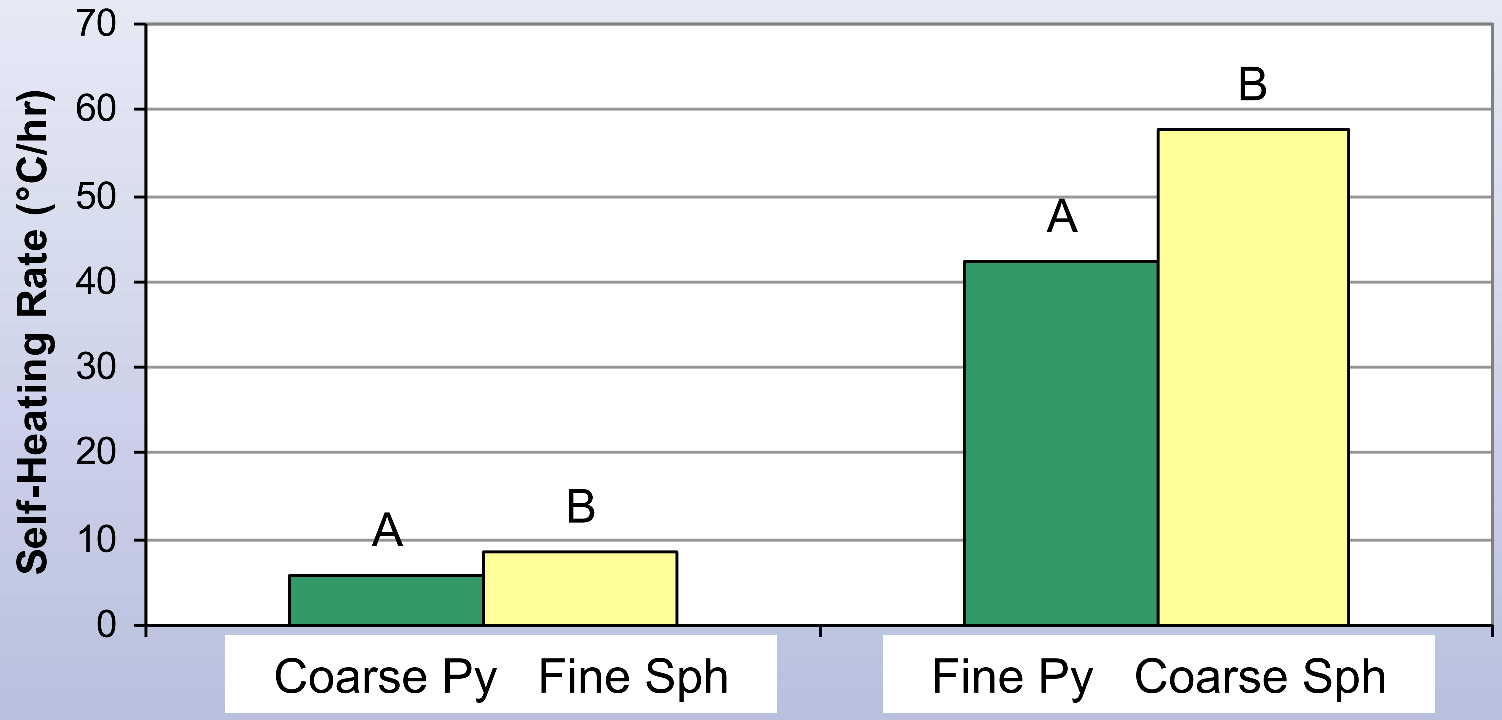


The Rest Potential Difference > 0.2 volts

Single minerals will not self-heat

Payant et al., 2009

Results for Mineral Mixtures: Rate Determining Reaction



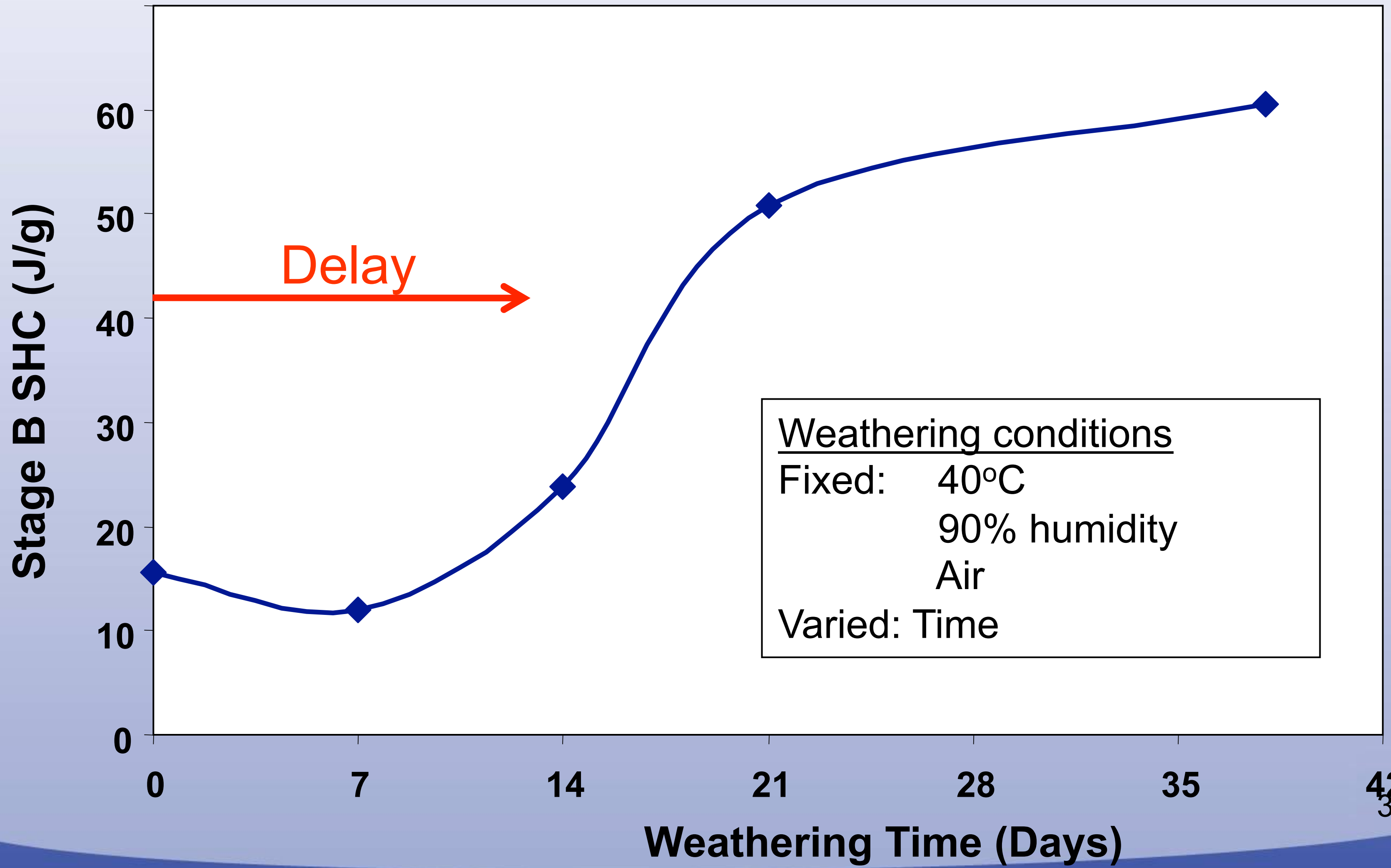
Mass 50:50

The reduction reaction (cathodic) is rate determining

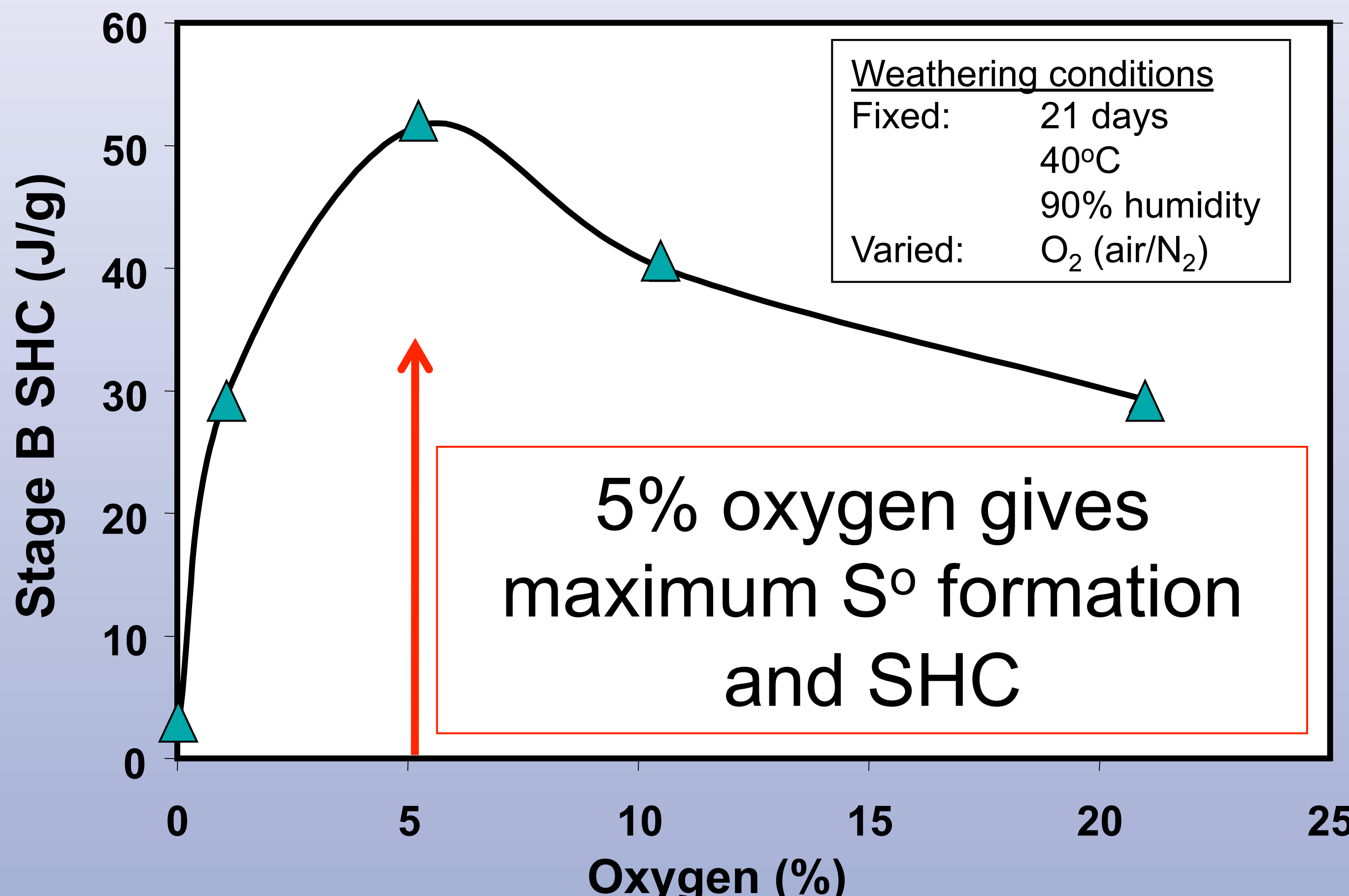
Payant et al., 2009

What other variables are important?

Time (weathering) on Stage B SHC
- Ni concentrate



Oxygen Level on Stage B SHC
-Ni Concentrate



Moisture Content on Self-heating Rate °C/hr

-sulphide tailings

Max heating rate at ~3% moisture

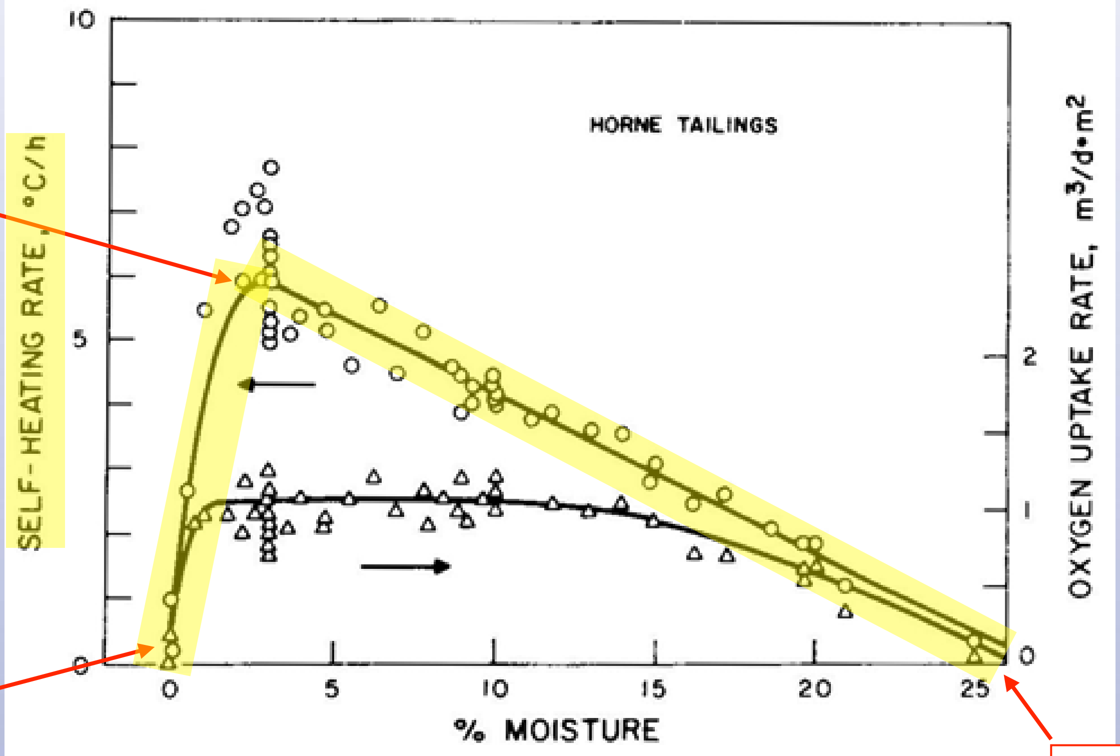


Figure 4. Effect of moisture content on the self-heating and oxygen uptake rates of Horne tailings.

"Bone Dry"

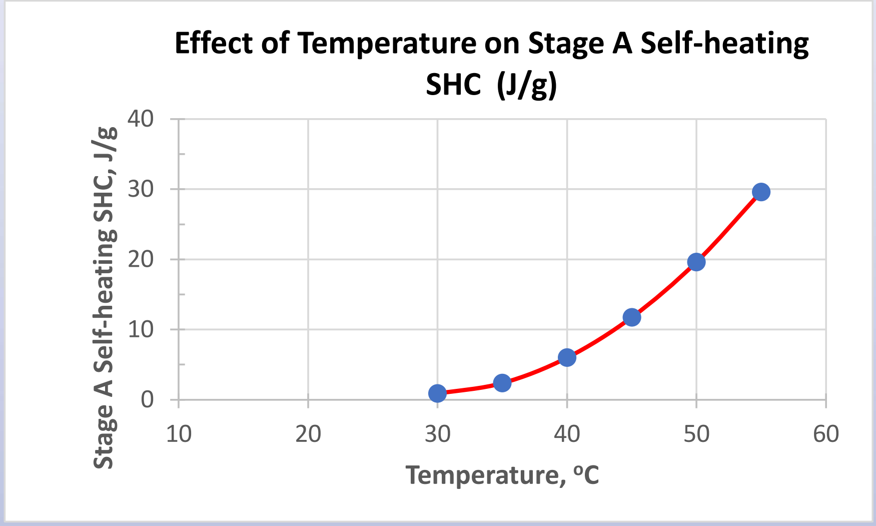
No moisture

Pore Saturation

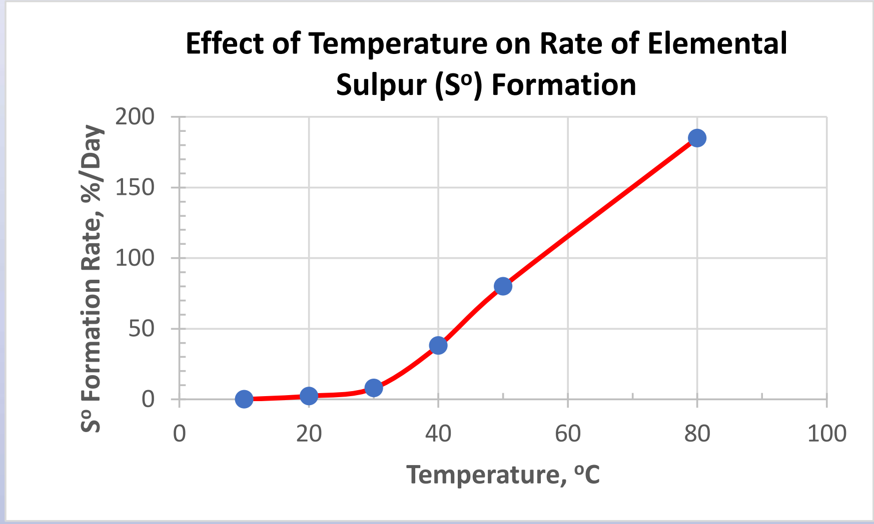
No oxygen

From 1982 IMPC paper by Rosenblum and Spira

Temperature on Self-heating rate and Rate of Elemental Sulphur Formation



Ni Concentrate at 3% moisture

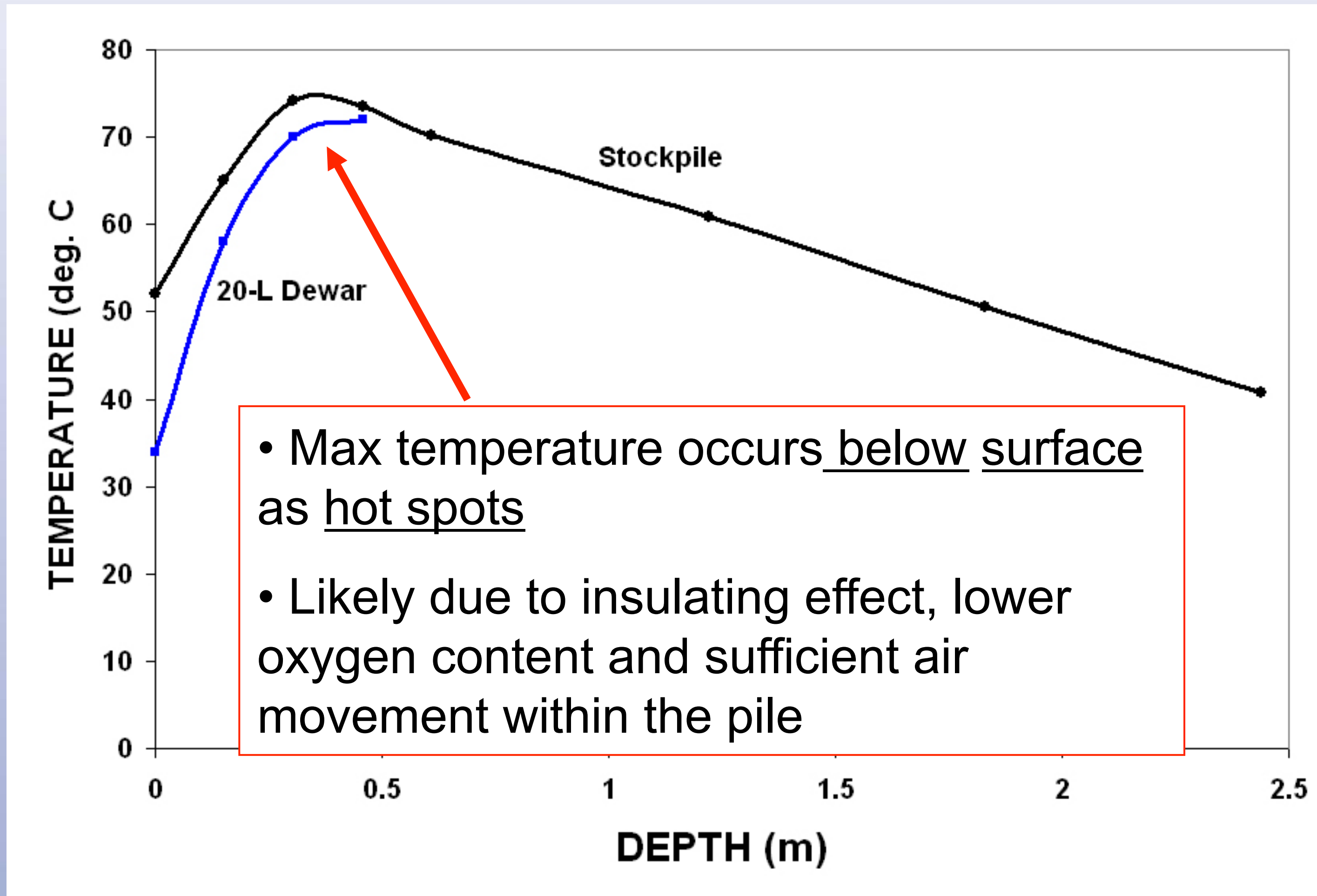


Pyrrhotite rich tails at 6% moisture

Self heating rate increases exponentially with temperature > 30°C

Production of elemental S increases dramatically > 30°C

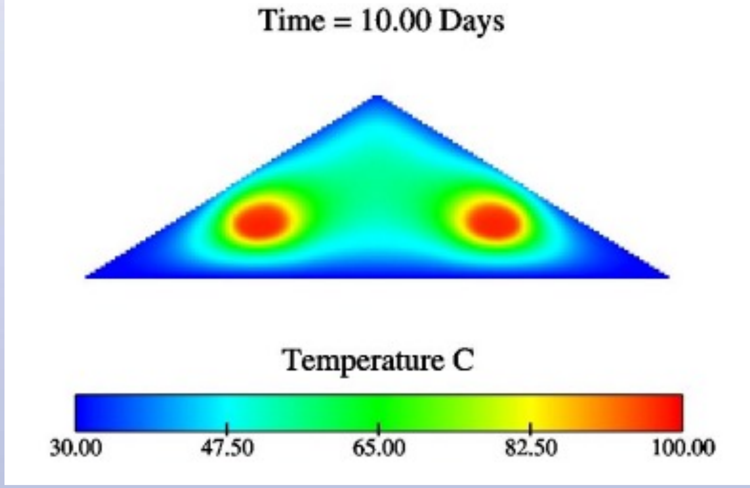
Permeability - Temperature profile with depth - maximum heating occurs below the surface



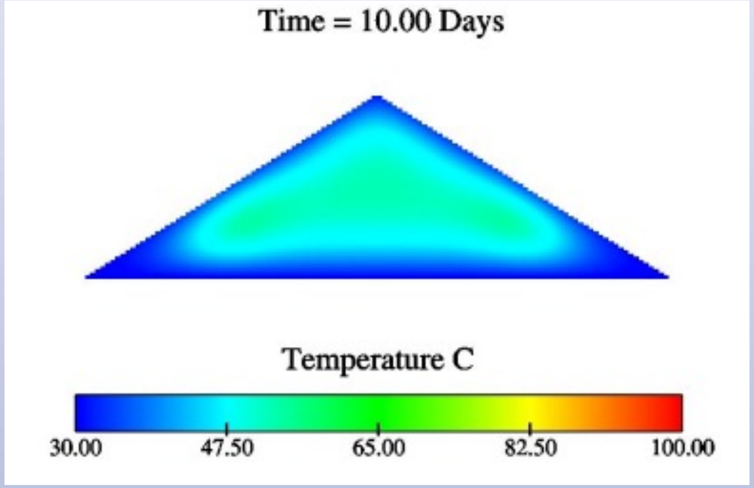
- Max temperature occurs below surface as hot spots
- Likely due to insulating effect, lower oxygen content and sufficient air movement within the pile

Segregation 0f Particle Sizes - increases permeability and risk of self-heating in stockpiles

Segregated Stockpile

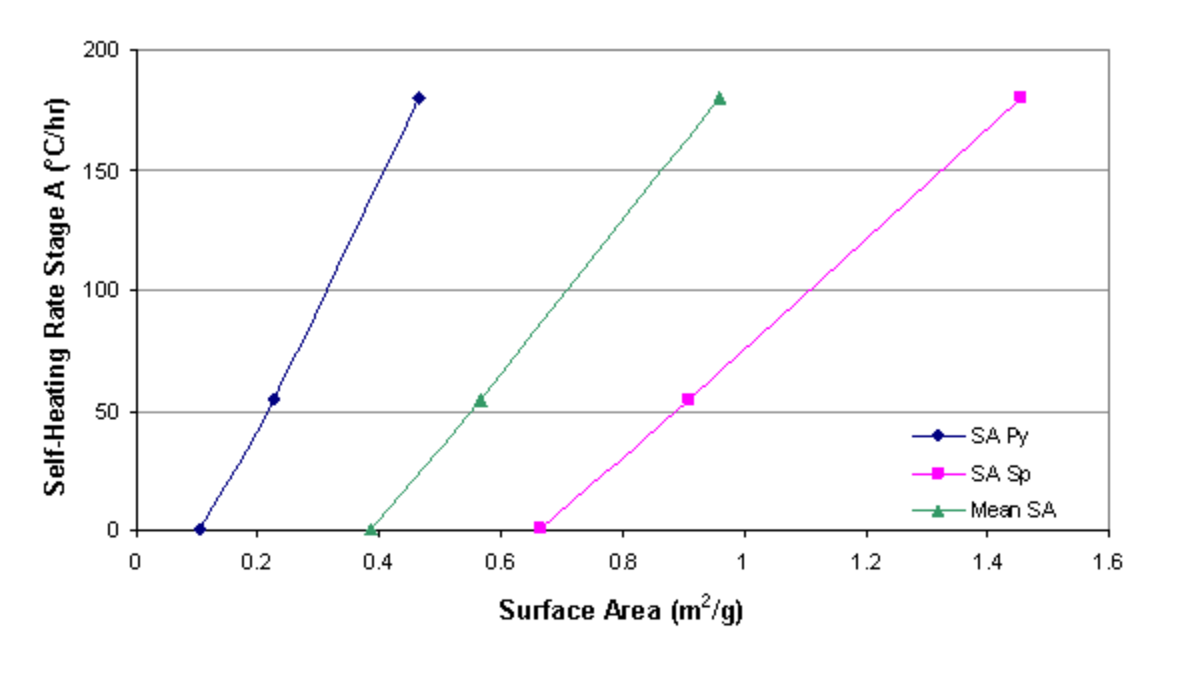


Uniform Stockpile



- Stockpile modelling by a client
- Segregation of concentrate pellets causes larger material to collect near outside bottom of stockpile

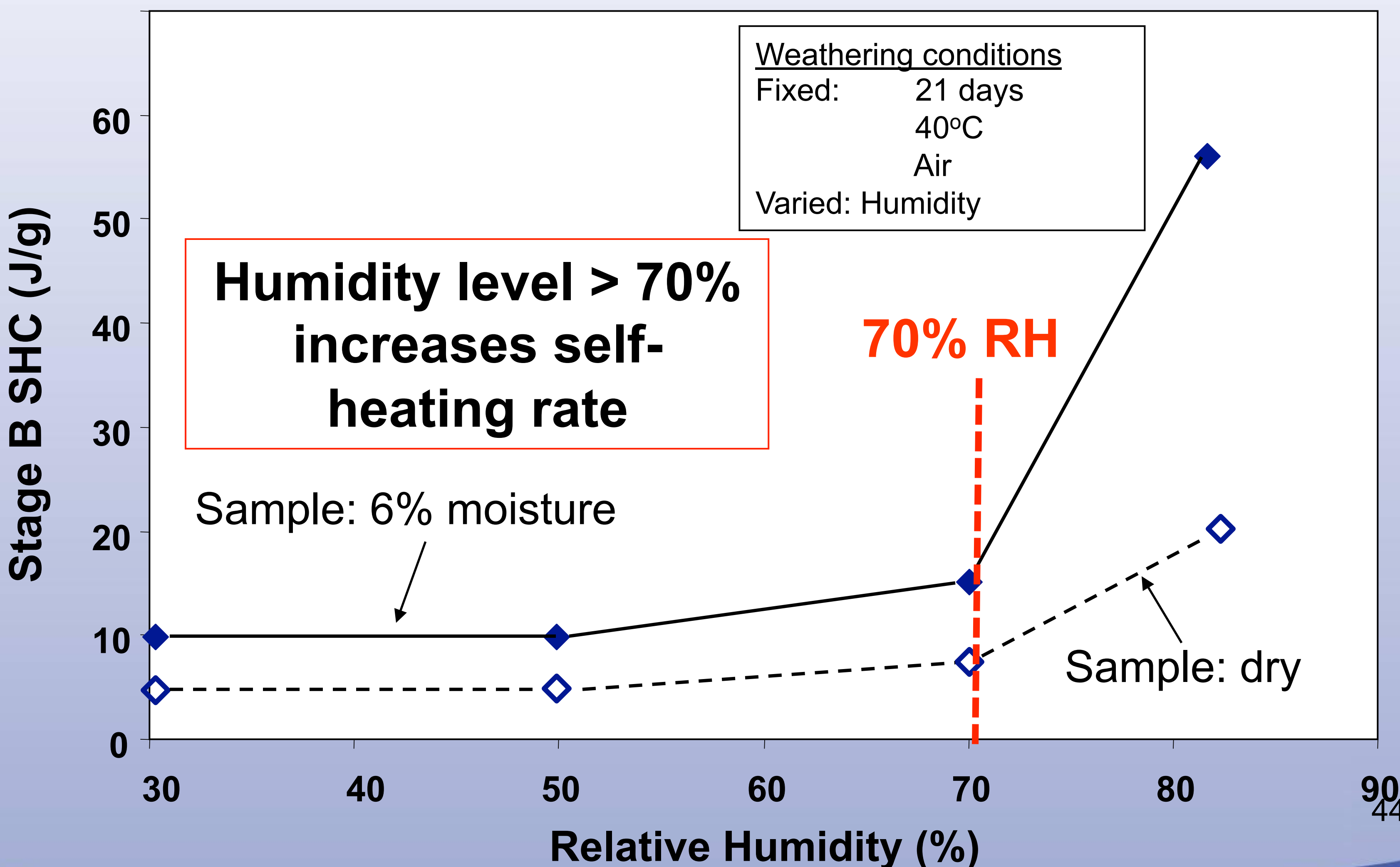
Particle Size (Surface Area)



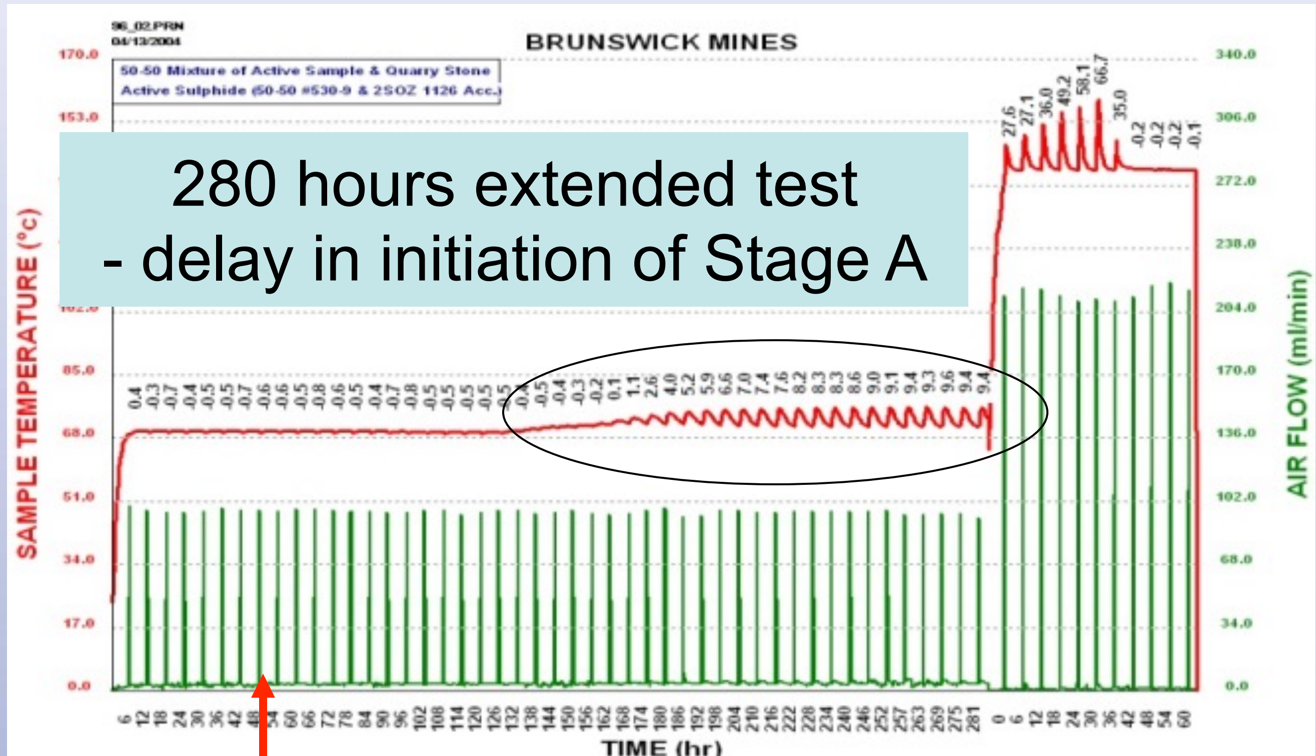
- Mixture of pyrite and sphalerite at different particle size P80
- Self-heating rate increases in proportion to the surface area of the minerals

Payant et al. *Min Eng 2012*

Relative Humidity (RH) of the Air
-Ni Concentrate



<u>Buffering Minerals</u> – delay onset of self-heating



48 hrs standard Stage A

Delayed reaction likely due to buffering of acid produced

Summary: Key Reaction Concepts

1. The initial reactions are electrochemical in basis
2. Moisture and oxygen are key to initial reactions
3. Optimum oxygen concentration is ~5%
4. Temperature >30 ^oC and Relative Humidity > 70% rapidly accelerate the Stage A reactions
5. Increased permeability increases heating in piles
6. Acid and H_2S generation play key roles in the Stage A sequence. H_2S generation results in S^o formation and release of heat
7. S^o oxidation results in SO_2 formation in Stage B and release of heat

Summary Continued

8. Some sulphide mixtures exhibit delayed heating (due to buffering minerals) and require a longer Stage A test
9. The "electrochemical model" requires a difference in the rest potential (> 0.2 volts) between sulphides for self-heating to occur.
10. Individual sulphides do not self-heat (pyrrhotite?)
11. Self-heating is proportional to the surface area of the relevant sulphide mineral particles
12. The rate limiting step is the reduction reaction at the cathodic mineral (so there needs to be sufficient cathodic mineral (e.g. pyrite)

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Thank You