First flush, 'reverse first flush' and 'partial first flush':

dynamics of short- and long-term changes in the quality of water flowing from abandoned, flooded deep mine systems

Paul L Younger[1] and Agnes Blachere[2]

[1] HERO Group, School of Civil Eng. & Geosci., University of Newcastle, UK (hero@ncl.ac.uk)

[2] CESAME Bureau d'Études, Fraisses, France

Overview

- Mine water rebound and water quality deterioration in deep mine systems
- The 'first-flush' and beyond
- Modifications of basic first flush model according to mine geometry:
  - Reverse first flush
  - Partial first flush
- Implications for long-term mine water quality management and wider relevance

Drop the cliché …

- The hackneyed view of acid rock drainage views the production of poor quality water as essentially a single, rapid process of congruent, oxidative dissolution of pyrite:

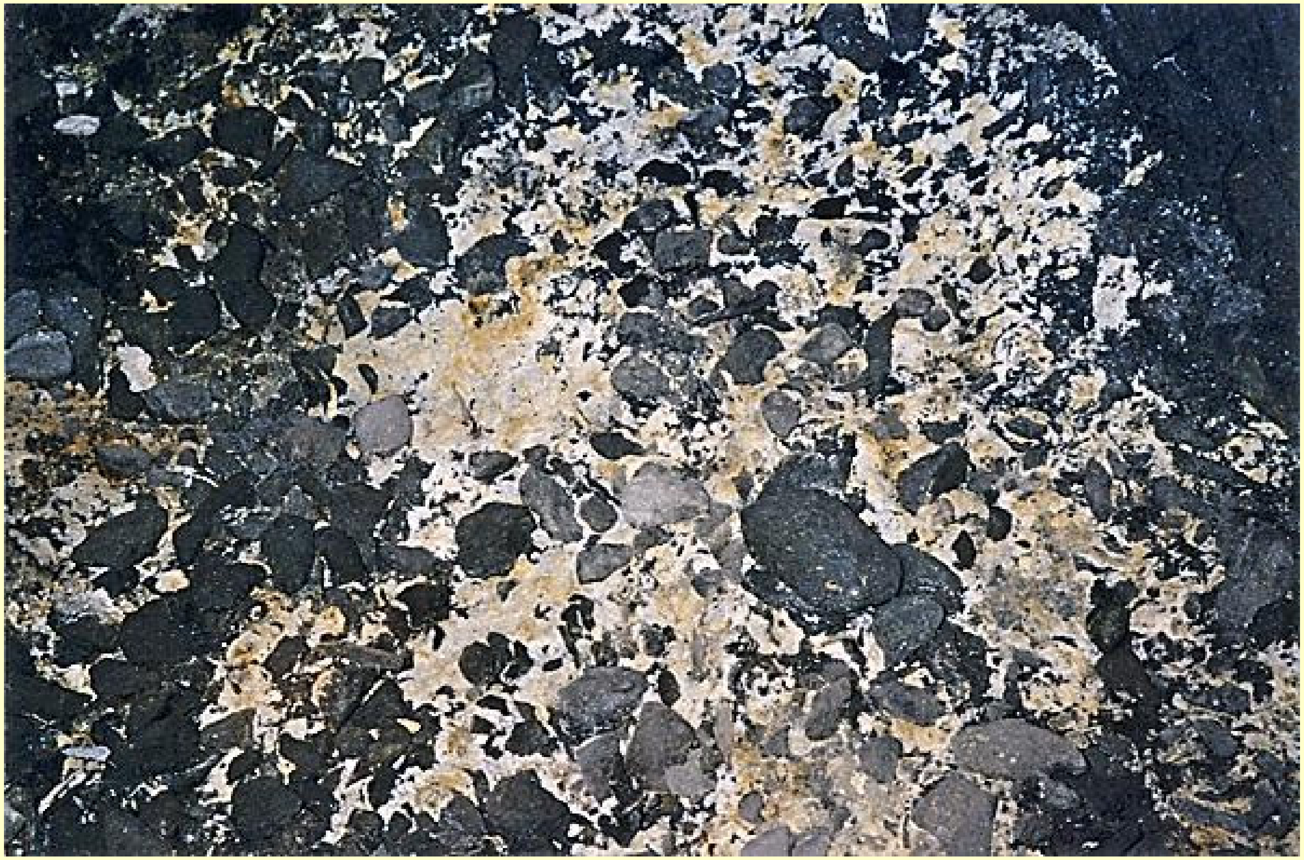
$$FeS_2 + 3.5\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

- This may be so in some surface mine systems located in humid areas with equable climates
- Elsewhere, and notably in deep mine systems, pyrite oxidation is more commonly *incongruent*, so that solid-phase oxidation products are stored above the water table

Storage of pyrite oxidation products in the unsaturated zone

- Fe and S stored as ferric / ferrous hydroxysulphate minerals (evaporites), such as:
  - melanterite ($FeSO_4.7H_2O$)
  - römerite ($Fe^{(2+)}Fe^{(3+)}_2(SO_4)_4.14H_2O$)
  - coquimbite ($Fe_2(SO_4)_3.9H_2O$)
  - copiapite $Fe^{(2+)}Fe^{(3+)}_4(SO_4)_6(OH)_2.20H_2O$)
- Role in seasonal storage and release of contaminants (Zn, Cd) in deep mines is well documented (e.g. Nordstrom *et al.* 2000, **Env.Sci.Tech.** 34: 254 258)
- Same class of minerals responsible for gross deterioration in water quality when deep mines are left to flood; not only release 'lattice metals' but also many adsorbed metals and protons

The hydroxy-sulphate time-bomb …

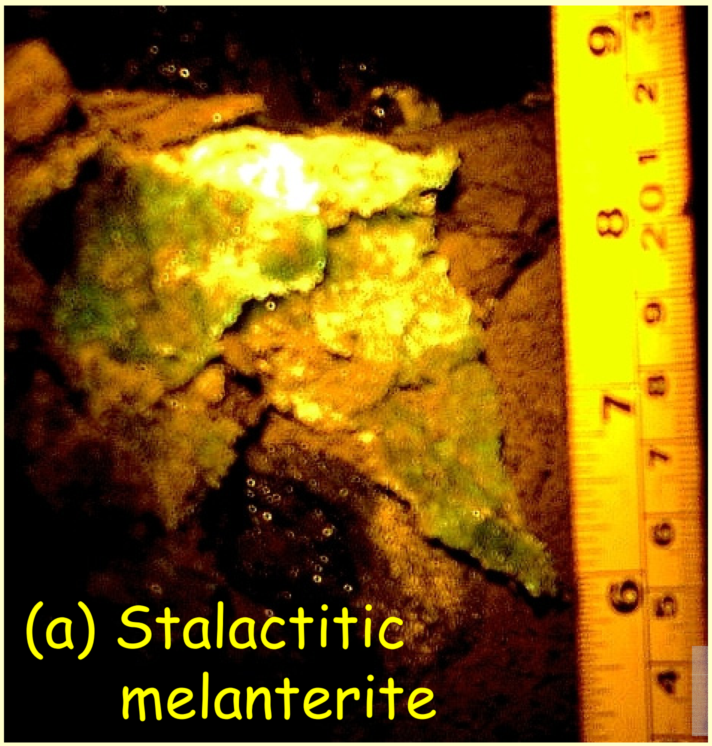


Mina de Raposos gold mine, Minas Gerais (Brasil)

Pyrite oxidation products (aluminocopiapite) cementing track ballast at the edge of a major roadway, 860m below ground

The hydroxy-sulphate time-bomb …

Blenkinsopp Colliery, Northumberland (UK)



Water quality deterioration during the flooding of deep mines

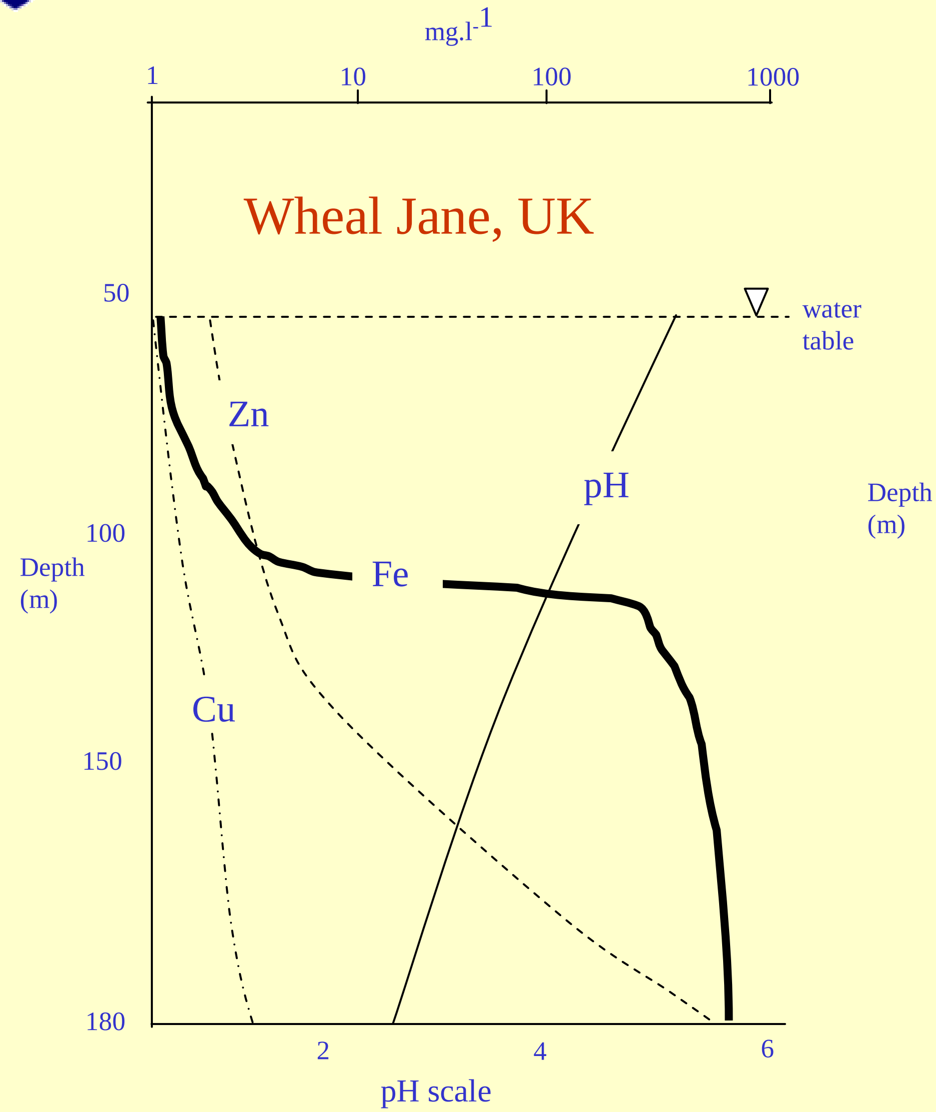
- Common observations (metalliferous mines and coal mines):
  - ten fold increases in dissolved Fe, SO_4, and other contaminants
  - intimate water rock interactions *do* promote natural attenuation, reflected in upper limits for some contaminants (e.g. 2500 mg/l SO_4 from gypsum equilibrium; sorption equilibria often limit Fe to 1500 mg/l (Coal Measures), 2500 mg/l (metalliferous ore bodies))
  - pH often drops from neutral to around 3

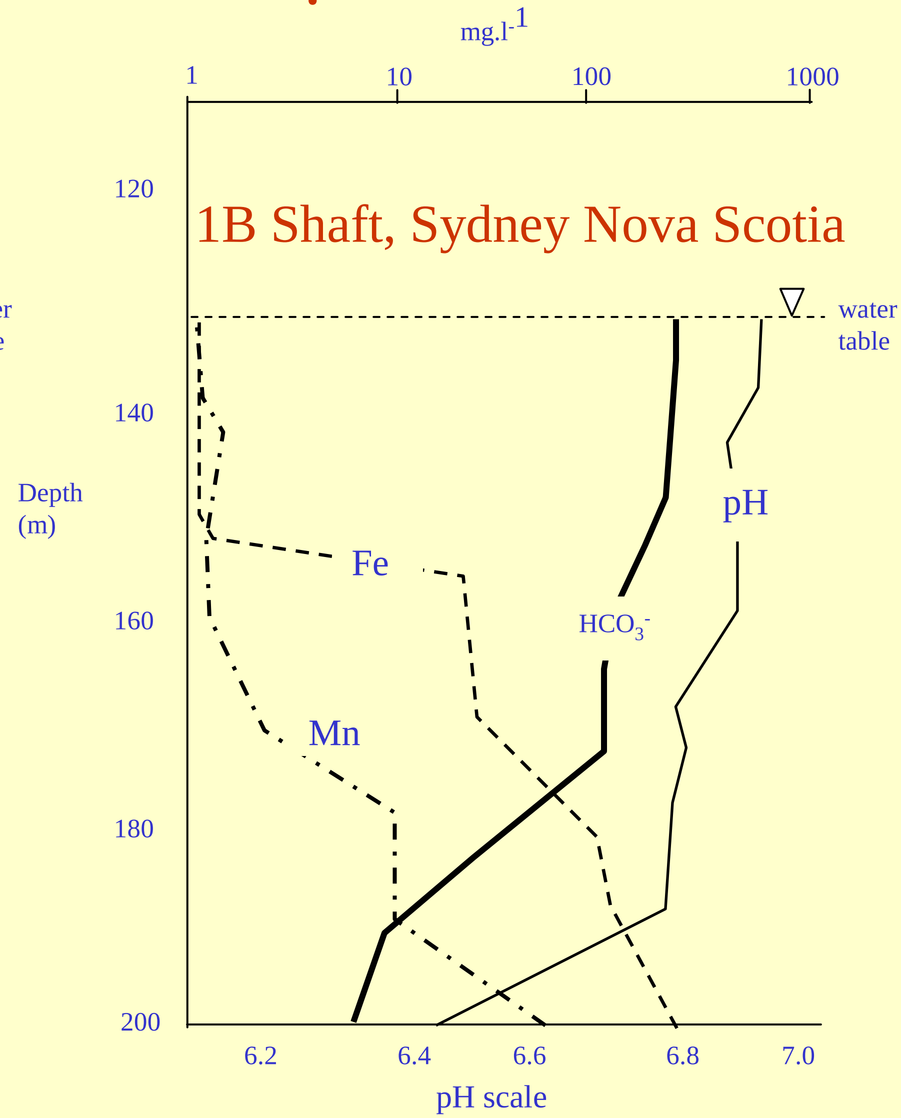
Hydrochemical stratification during rebound

- As the water table rises in flooding workings, it is commonly found that the quality of water in the workings stratifies in terms of total dissolved solids and individual contaminants
- TDS variations result in viscosity and / or density layering of water column
- Stratification is favoured by the hydraulics of a flooding system with few discrete outflow points
- It is important to recognise that stratification is generally lost once pumping or natural overflow commence (failure to recognise this can cause red streams <u>and</u> red faces!)

(Nuttall and Younger 2003 J.Contam. Hydrol. (*in press*))

Stratification Examples

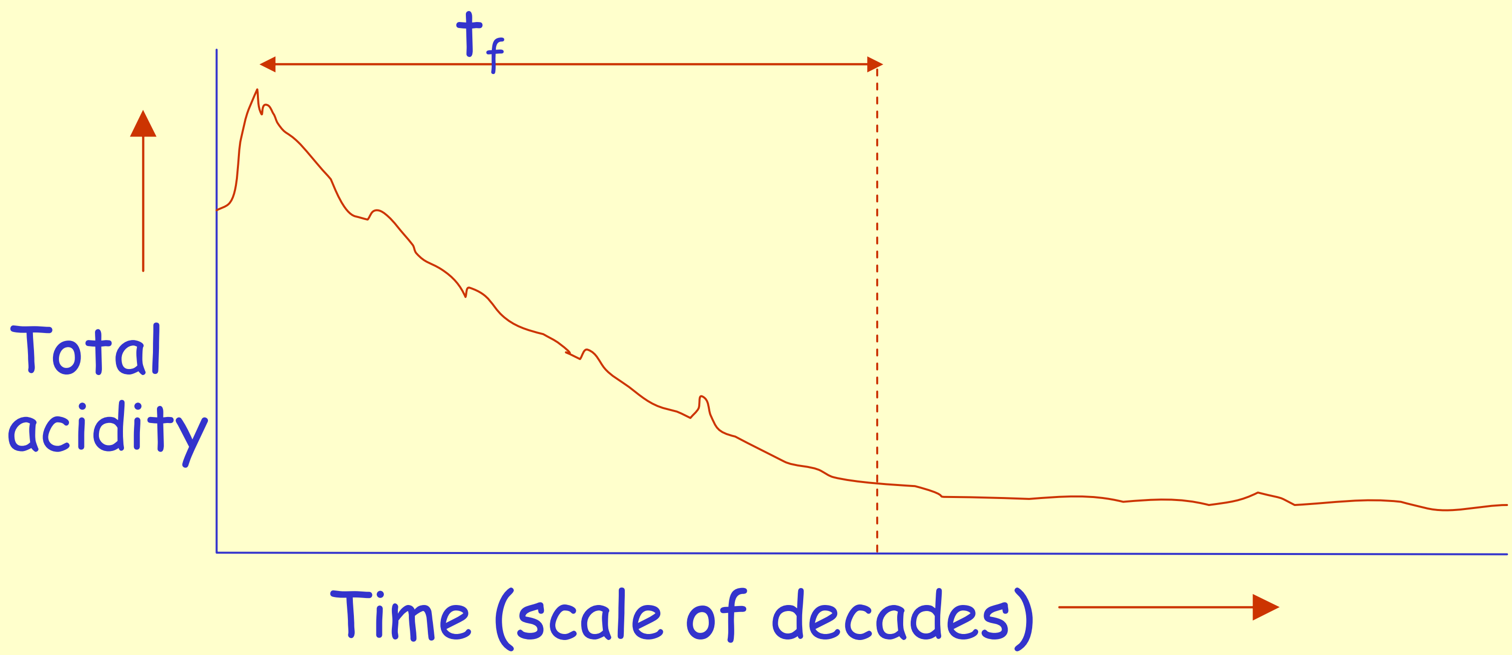




After discharge commences …

- Common temporal patterns:
  - Rapid breakdown of stratification, with highest concentrations of contaminants reached soon after overflow commences (e.g. after one shaft volume)
  - Exponential decrease in contaminant concentrations during a 'first-flush' period, as salts dissolved during flooding are gradually flushed from the system
  - After the first flush, long-term persistence of an asymptotic level of pollution, controlled by the balance between:
    - sulfide oxidation above the minimum water table position and
    - buffering reactions (carbonate, silicate) which (unlike sulfide oxidation) occur throughout saturated zone

"The First Flush"



Models of first flush

- Classic analytical approach – feasible but limited real-world applicability
- Full numerical modelling – notionally feasible, but given complex hydraulics would require enormous cpu time
- Empirical models – based on hydrological principles; easy to use

Analytical Model of First Flush – Modified Sauty Solution to ADE

- $C(t) = 0.5\, C_o\, [\mathrm{erfc}(\{L - v_a\, t_w\}/\{2(Dt_w)^{0.5}\}] + C_a$
- Where:

  $C(t)$ = concentration at outflow from mine at time t (i.e. the elapsed time since the mine began to overflow)

  $C_o = C_p - C_a$

  C_p = peak concentration at start of first flush

  C_a = steady concentration at end of first flush

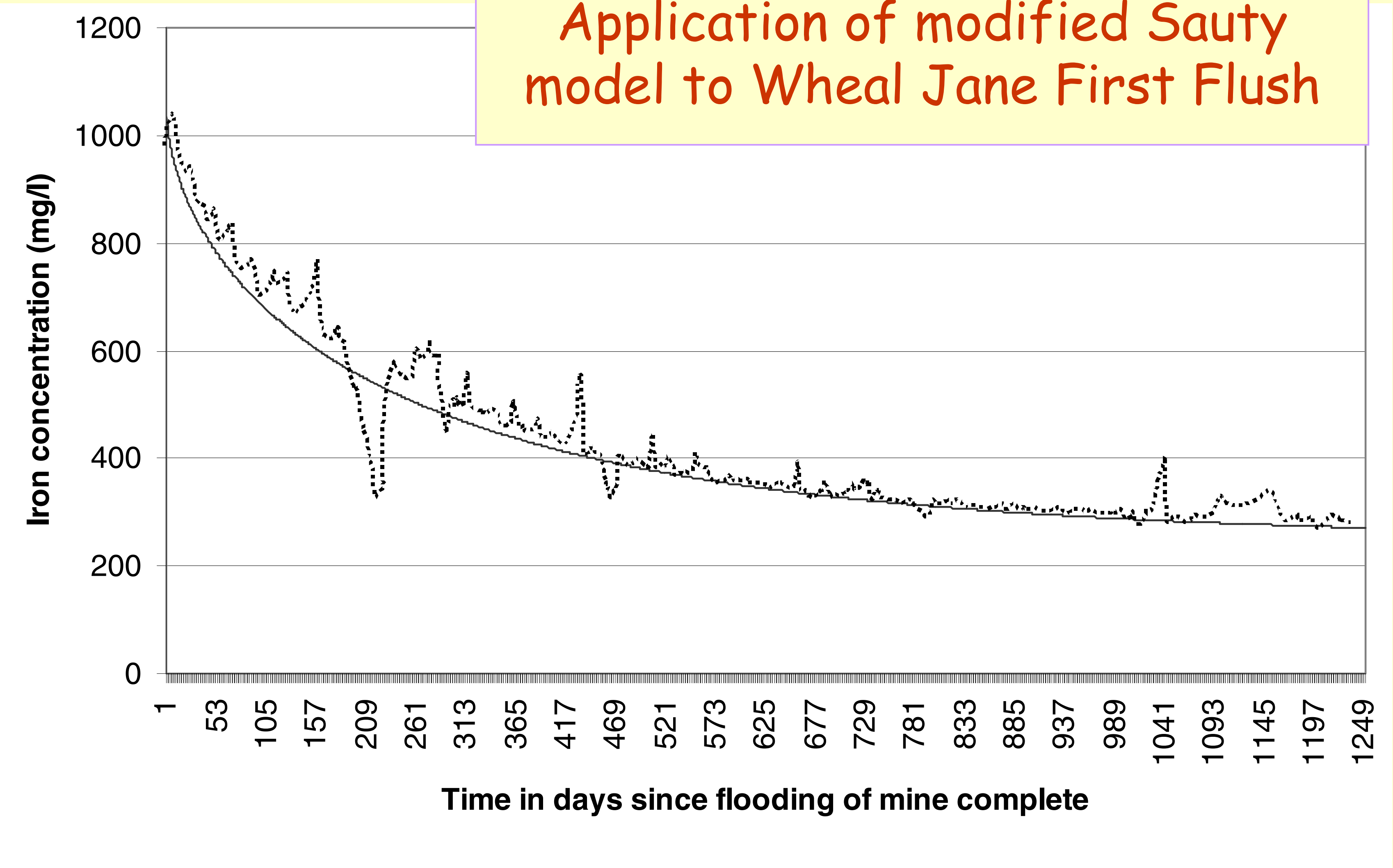
  v_a = average groundwater flow velocity within the mine system (L/T)

  t_w = "working time", the difference between the total length of the main flushing period (found on a trial-and-error basis) and time since overflow commenced

  D = longitudinal dispersion coefficient ($L^2.T^{-1}$)

  (erfc is the complementary error function)

Application of modified Sauty model to Wheal Jane First Flush



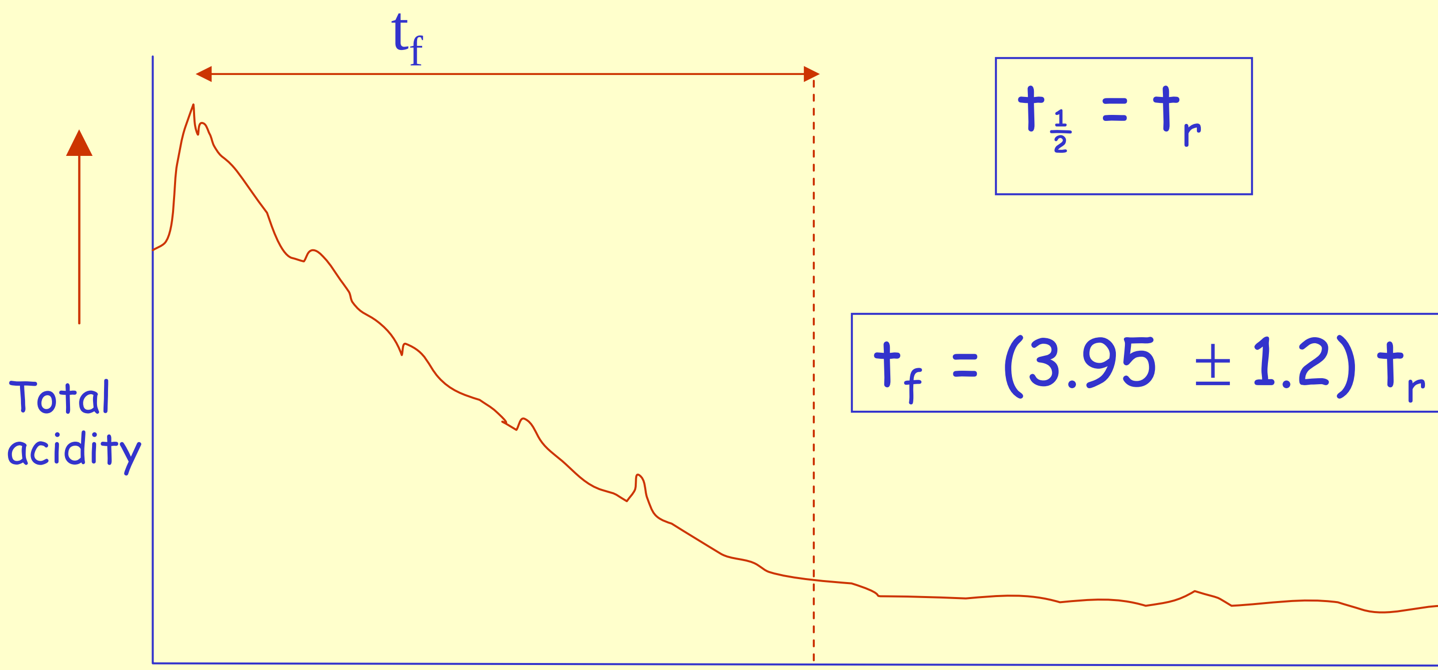
Empirical model for first flush

- Controls on first flush:

  Hydraulic turnover rate

  = F (total pore volume / rate of recharge)
- Closely resembles controls on rebound rate (notwithstanding loss of head-dependent mine water sources as water table rises)
- Observations since 1960s suggest exponential first-flush with half-life = duration of preceding rebound period

Empirical model for first flush



$$t_{\frac{1}{2}} = t_r$$

$$t_f = (3.95 \pm 1.2)\, t_r$$

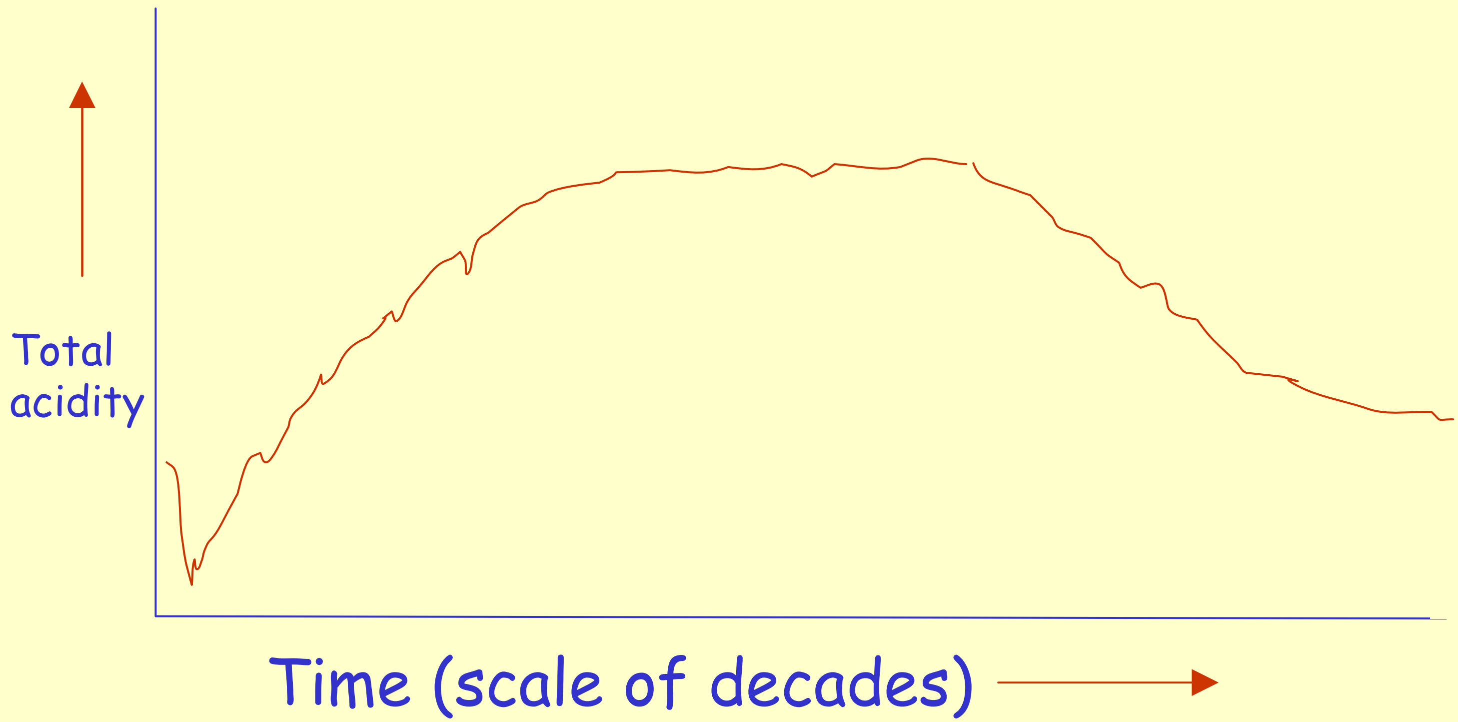
Time (scale of decades) →

(Jl. Contam. Hydrol., 44, pp 47 - 69 (2000))

Reverse First Flush

- Rare product of peculiar hydrogeological circumstances
- Best quality water flushed first, with poorer quality water following later
- Occurs where sulfide-rich strata are shallow, but all overflow must be routed via very deep flow paths (can be induced by pumping; e.g. Polkemmet Colliery, Scotland)
- Principal current example: South Crofty Tin Mine, Cornwall (UK)

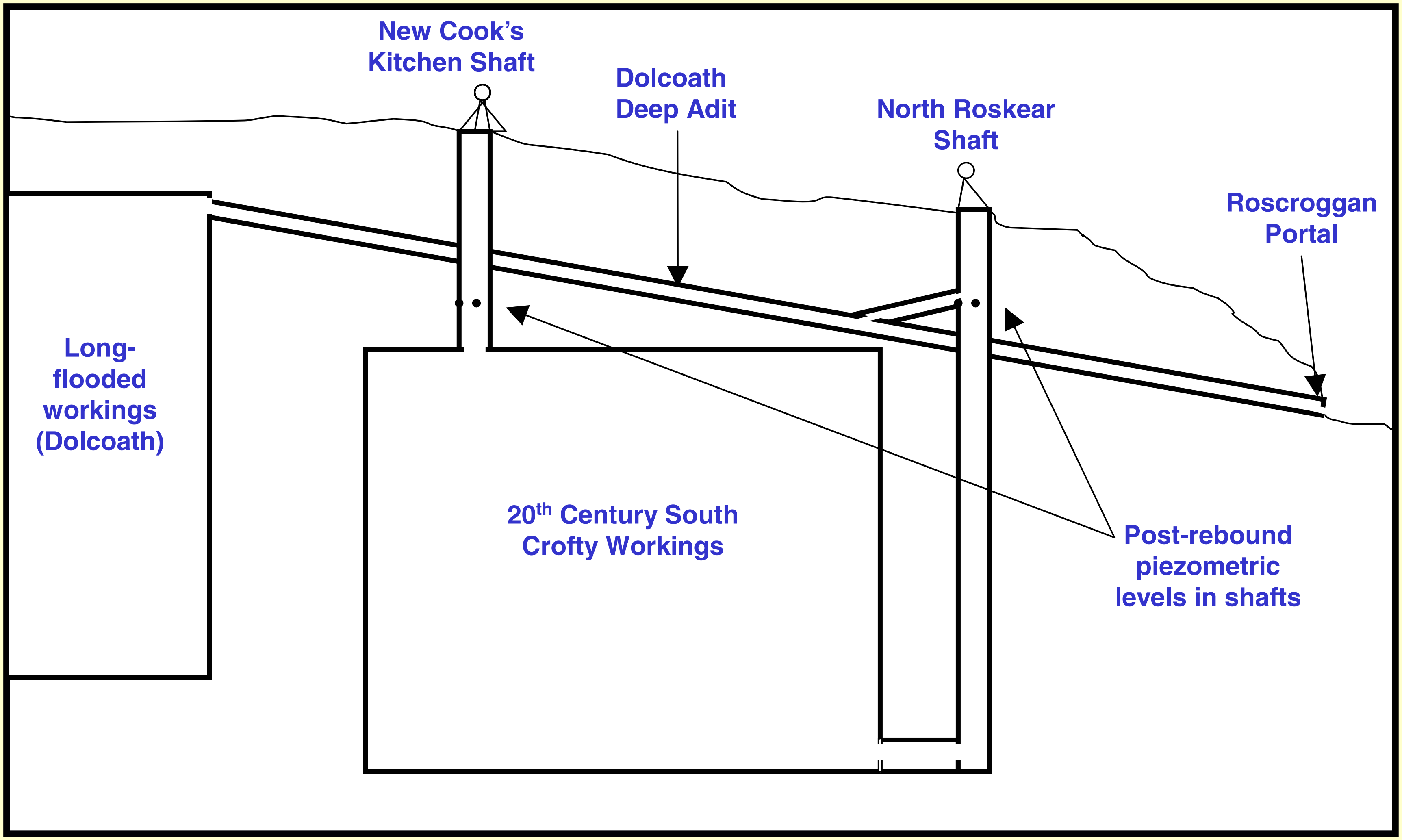
"Reverse first flush"



South Crofty Tin Mine

- Shaft water column sampling has revealed that:
  - top of water column has become acidic during rebound through relatively shallow zone of copper sulphide mineralisation
  - deeper waters (in zone of cassiterite and metasomatic haematite) remain circum-neutral
- However, shallow acidic water must flow down to great depth before rising to surface through North Roskear Shaft
- Gradual deterioration in quality of overflow water over time now being experienced ('reverse first flush')

South Crofty: sketch x-section



S. Crofty: Dolcoath Deep Adit

Stacked 'deads' near Mayne's Shaft

1830s copper workings (Wheal Susan)

Decant route from N Roskear Shaft to Dolcoath Deep Adit

Roskear branch backfilled during 1950s adit maintenance works

Crofty's last workings - mining out the Roskear branch backfill to prevent hazardous ponding

Crofty's built-in 'clarifier' – every adit should have one!

Entire flow of adit disappears down the Doctor's Shaft

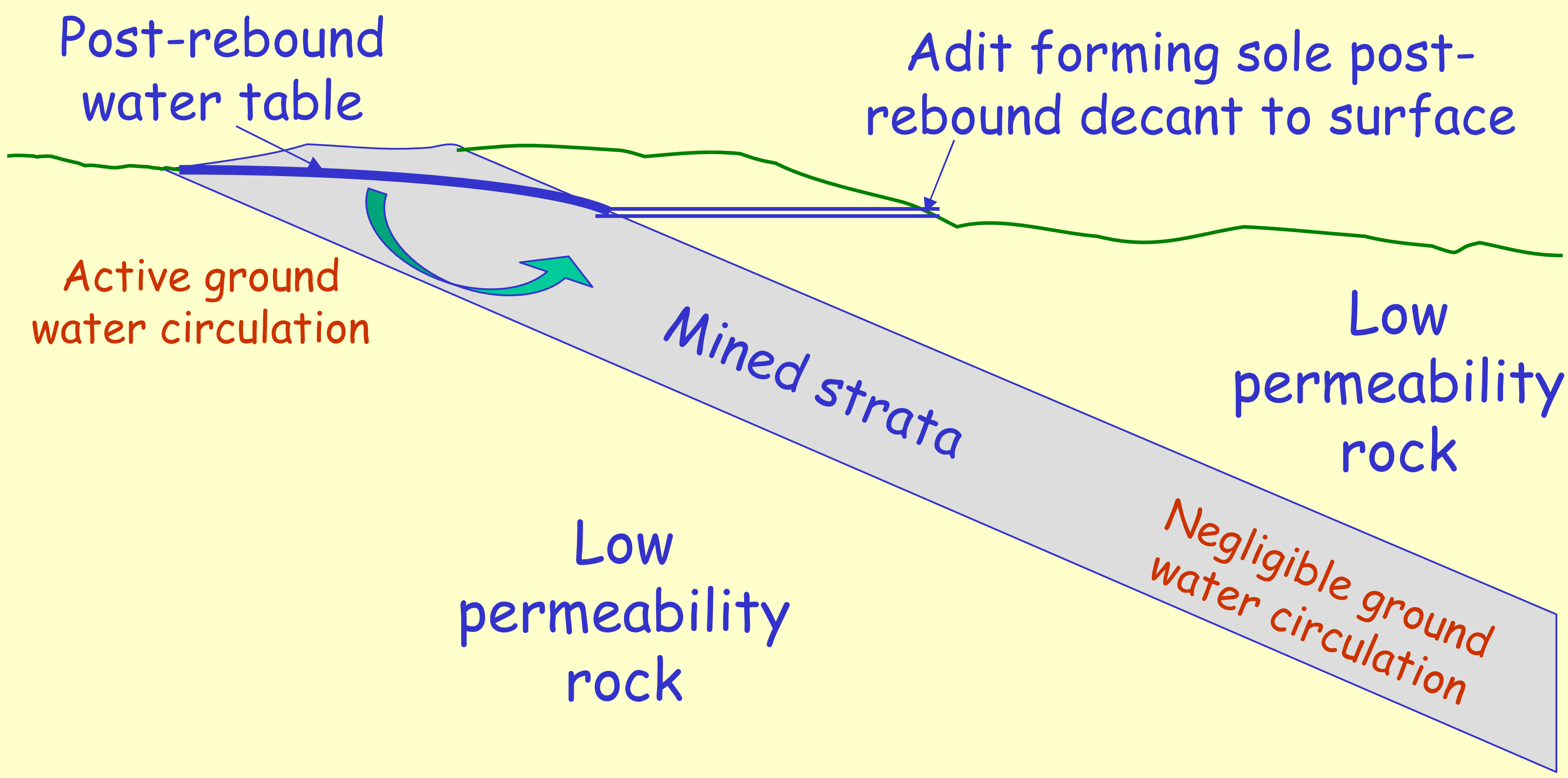
4 hours later, only 200m further outbye, water emerges back into adit from Daylight Shaft

Outflow from portal 400m down-stream

"Partial first flush"

- Application of original empirical model to mines in the Loire and Lyon coal basins (France) highlighted the need for customisation depending on the specific configuration of mine workings
- In particular, modifications have been proposed to take account of 'dead-end' mined porosity
- The recharge rate thus becomes the divisor of only part of the total void volume ('partial flush')
- This modification, which is easily implemented using mine survey evidence, greatly improves the predictive accuracy

System with 'dead-end' mine void porosity, prone to partial first flush



Partial first flush model

- Found to be especially applicable to very large systems in which a large proportion of the workings lie down-gradient from the final surface decant / pumping point
- Where original model states:

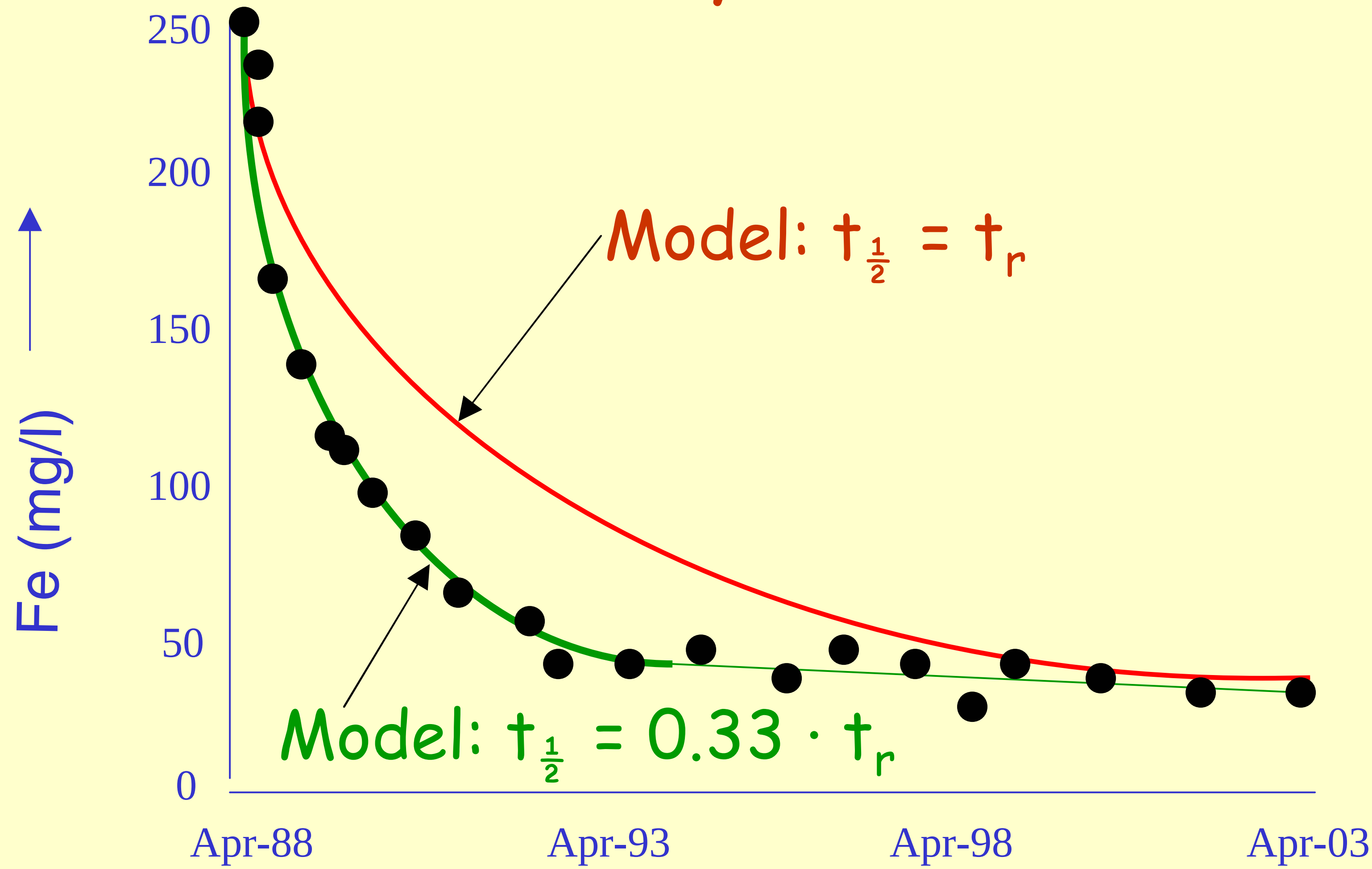
$$t_{\frac{1}{2}} = t_r$$

- Modified model is:

$$t_{\frac{1}{2}} = \nu \cdot t_r$$

where ν can range from 0.1 for very large 'dead-end' systems to 1 (i.e. original model)

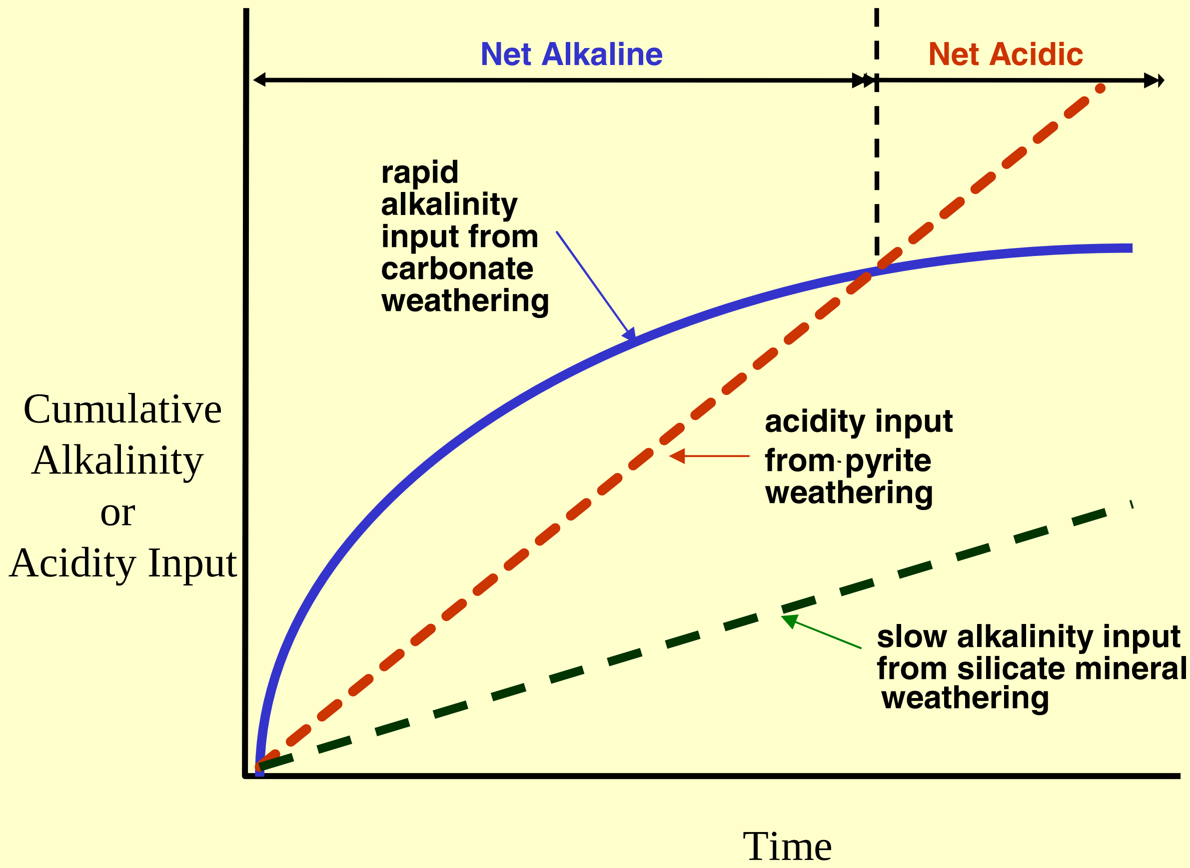
Example: Fendue Lyon Colliery (France)



Beyond the first flush …

- A long term handicap race:
  - Sulfides only oxidise significantly above water table; silicates and carbonates dissolve above and below water table
  - Kinetics of weathering are also unequal:

    carbonates > sulfides > silicates
  - Relative proportions of sulfides versus carbonates / silicates weathering determines long term post flush quality
  - This in turn depends primarily on mineralogy and hydrology of the system in question



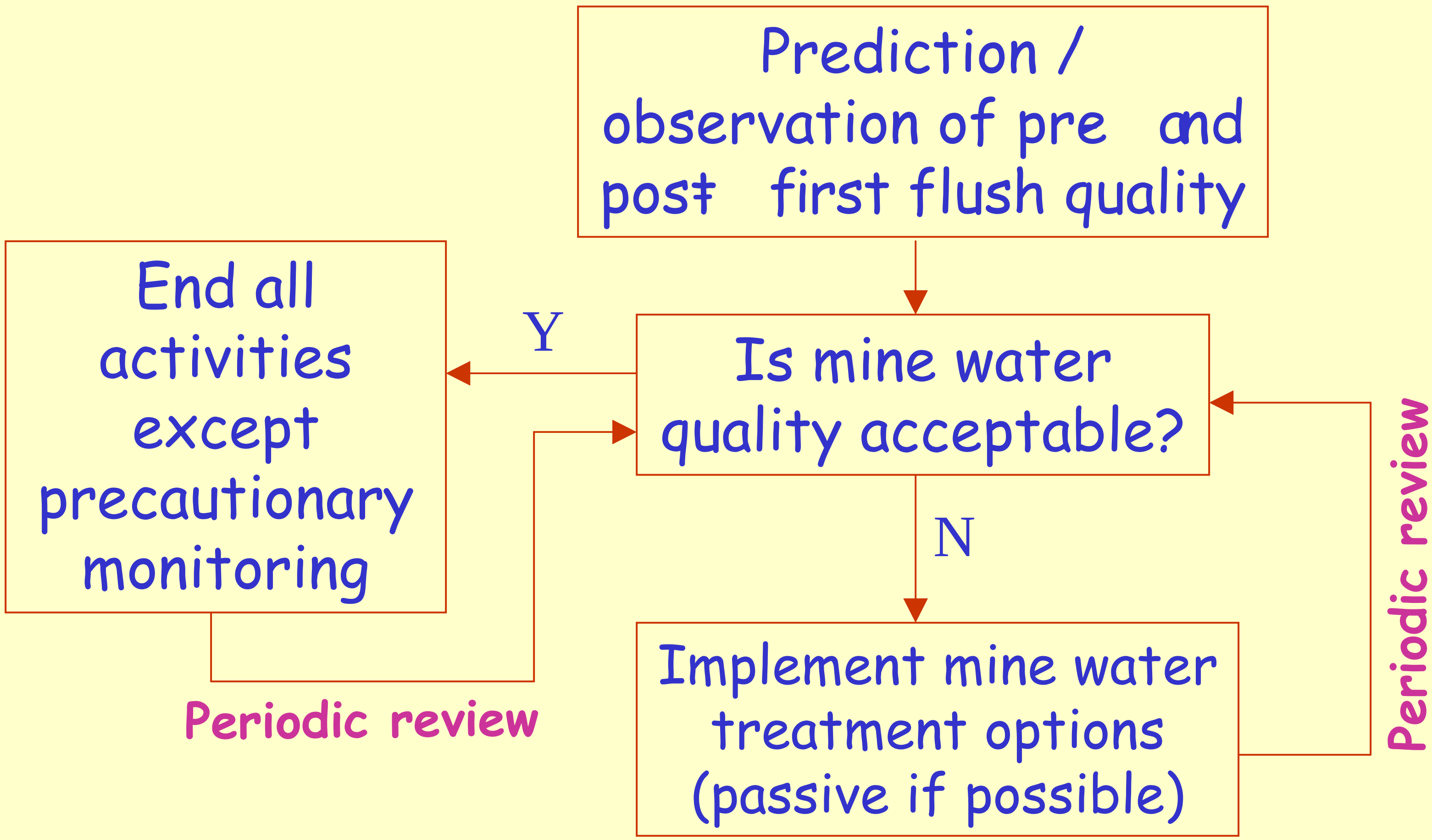
- Initially, carbonate (e.g. ankerite) weathering is brisk, providing much alkalinity
- Later, depletion of carbonates leads to pH drop as water becomes acidic
- Eventually, pyrite will be depleted and water becomes alkaline again due to sustained silicate weathering

Wider relevance

- Same concepts applicable (with some adjustment) to:
  - newly-flooded pit lakes
  - mine wastes newly subjected to water covers
- Obviously differences in hydraulic geometry must be taken into account
- Should be easier to artificially accelerate flushing in these surficial systems than in deep mine systems

e.g. Westfield opencast (Scotland): *integrating pit lake rebound with pyritic waste submergence*

Remedial strategy



Conclusion

- Recognition and prediction of flushing phenomena following deep mine abandonment is crucial for ensuring adequate post-closure planning
- Empirically-based models showing increasing reliability for such purposes
- Mine system geometry exerts strong control on flushing patterns
- Long-term water quality prediction demands far better integration of mineralogical and hydrological studies than we currently achieve

Christmas present from Europe

- Free download of EU's new Engineering Guidelines for Passive Remediation of Acidic Mine Drainage from:

  www.piramid.org

- And for the New Year … Look out for 'Mine Water 2004' (Newcastle, Sept 20 – 25th 2004) – abstracts due 16-1-04:

  www.IMWA2004.ncl.ac.uk

Season's Greetings …