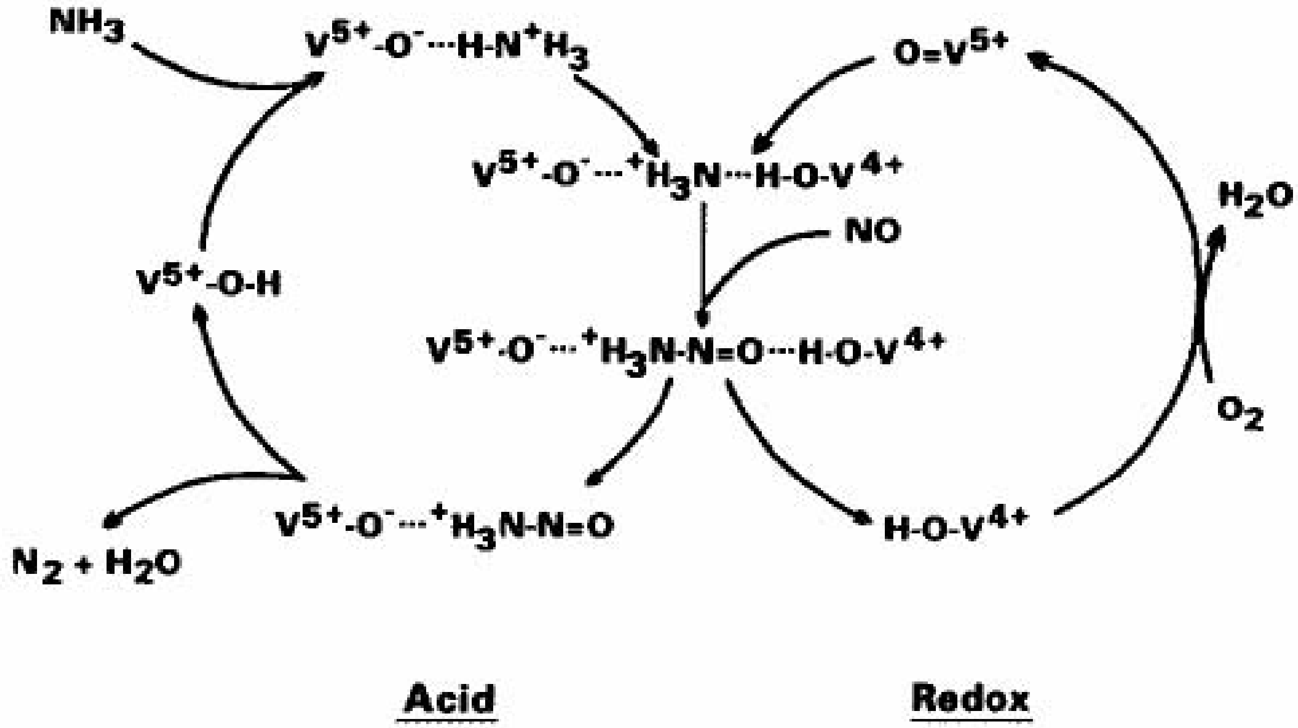
Reinhold Environmental Ltd.

2009 NOx-Combustion Round Table & Expo Presentation

February 9 & 10, 2009, Cleveland, OH

Comparison of Deactivation Rates of Different Catalyst Types



WPCA/PCUG NOx Round Table 2009
Cleveland, Ohio

Hans Hartenstein **Ed Healy**

EVONIK INDUSTRIES SOUTHERN COMPANY

Catalyst Deactivation Basics

Three different types of catalyst deactivation mechanisms:

- **Thermal deactivation due to rutilization as a result of overheating the catalyst – same for all catalyst types and makes that use TiO_2 as ceramic substrate.**

- **Physical deactivation by means of:**
  - **Cell and/or pore pluggage, i.e. fly ash, LPA, etc.**
  - **Surface blinding layers i.e. $CaSO_4$, eutectics, etc.**

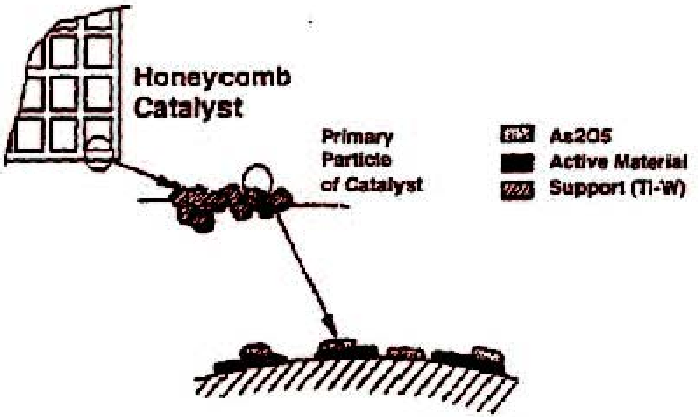
  Same for all catalyst types and makes as caused by flue gas and/or fly ash characteristics.

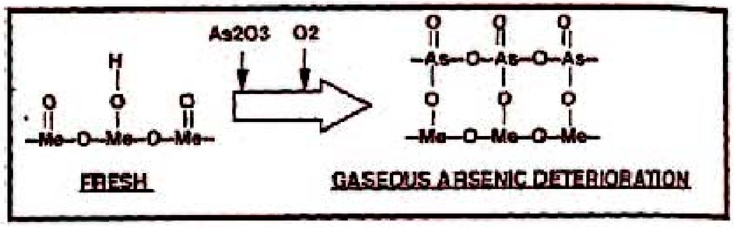
- **Chemical deactivation as a result of the reaction of flue gas constituents with the catalyst's catalytically active centers mostly consisting of V_2O_5.**

Chemical Catalyst Deactivation

Chemical catalyst deactivation is primarily caused by the reaction of cation species in the flue gas with catalytically active V_2O_5. The main catalyst poisons in coal are:

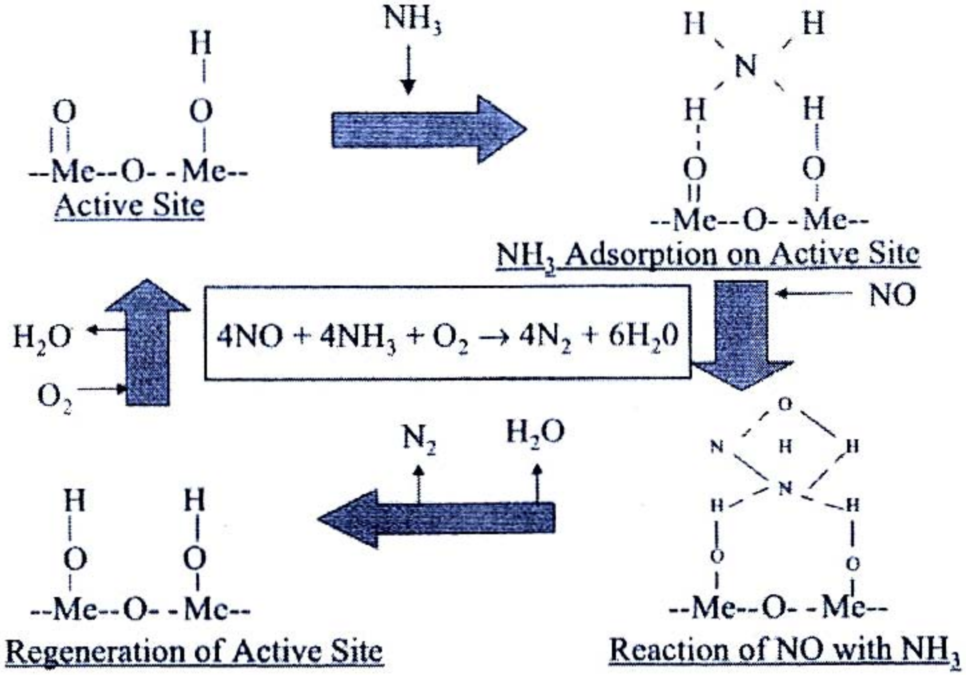
- **Non-metals, mainly phosphorus (P) as gaseous P_4O_6**
- **Alkali metals, mainly sodium (Na) and potassium (K)**
- **Alkaline earth metals, mainly calcium (Ca) magnesium (Mg) and to a lesser extent barium (Ba)**
- **Metalloids, mainly arsenic (As) as gaseous As_2O_3**



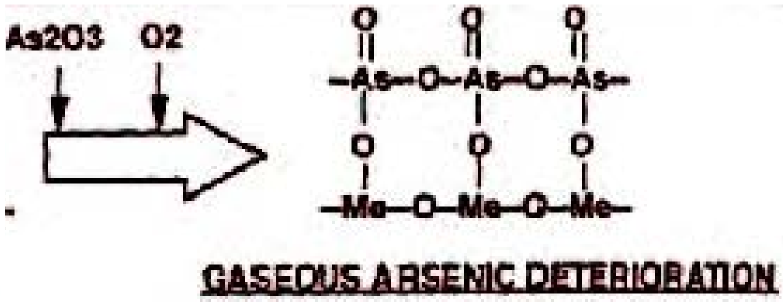


Chemical Catalyst Deactivation

Chemical deactivation follows the same principle regardless of type and make of SCR catalyst containing catalytically active V_2O_5 as the main ingredient. All known SCR catalysts commercially used in coal-fired units fall in this category.



Chemical deactivation of the catalytically active V_2O_5 sites by e.g. arsenic.



Chemical Catalyst Deactivation

In conclusion, theory suggests that all commercially used SCR catalyst regardless of type and make deactivates chemically the same way and also at the same rate when exposed to the same conditions including:

- **The same flue gas composition and temperature.**
- **The same basic SCR reactor design (same Lv).**
- **The same location (layer) within the SCR reactor.**

However, various claims to the contrary were made over the years, especially related to arsenic poisoning including:

- **"*Arsenic resistant*" catalyst, e.g. through addition of MoO_3.**
- **"*Arsenic tolerant*" catalyst, e.g. through migration of arsenic to center of thin wall.**
- **"*Arsenic proof*" catalyst, e.g. by means of tri-modal pore structure.**

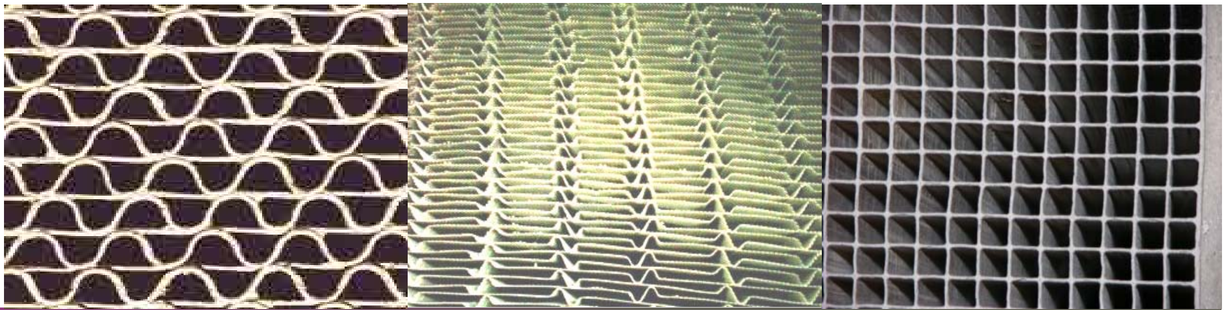
EVONIK INDUSTRIES

SOUTHERN COMPANY

Database for Actual Deactivation

- **Southern Company has 14 high-dust SCRs in Alabama, Florida and Georgia operational since the early 2000's.**
- **Evonik has 17 high-dust SCRs in Germany operational since 1987.**
- **Evonik has managed more than 30 high-dust SCRs in Florida, Illinois, Indiana, Kentucky, Maryland, New Jersey and New York some operational since 1993.**

These units have / had all types (corrugated, honeycomb, plate) and makes (Argillon, BASF, CERAM, Cormetech, Haldor Topsœ, Hitachi, IHI, KWH) of regenerated and/or new catalyst installed within the same reactor at the same time.



EVONIK INDUSTRIES

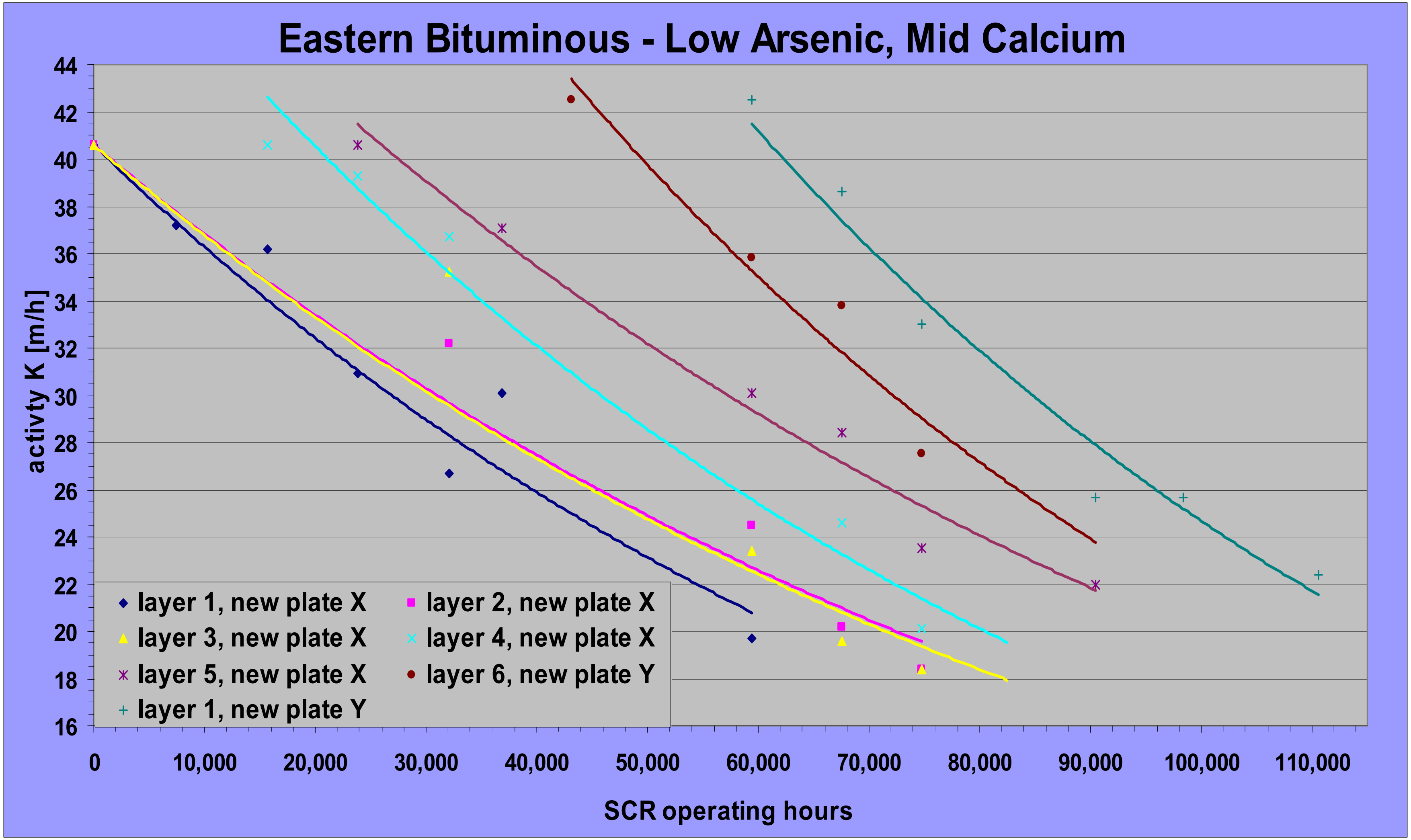
SOUTHERN COMPANY

Database for Actual Deactivation

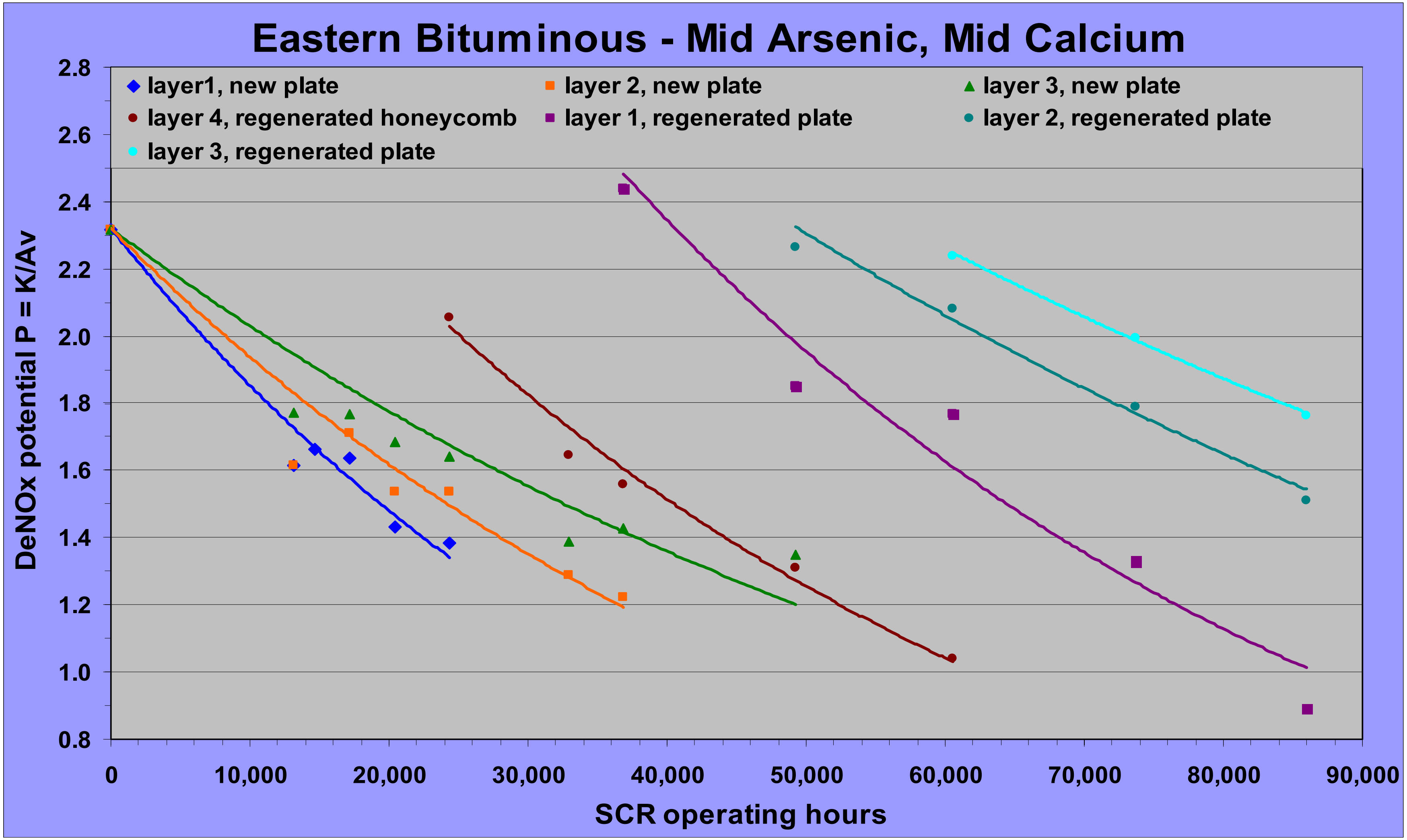
Differentiation according to catalyst poisons can results in the following categories:

- **low arsenic, mid calcium – e.g. Northern Appalachian**
- **mid arsenic, mid calcium – e.g. Eastern Kenntucky**
- **high arsenic, low calcium – e.g. Southern Illinois Basin and Northern Alabama**
- **high calcium, high alkali – e.g. PRB**
- **high alkali, high phosphorus – e.g. biomass, lignite**

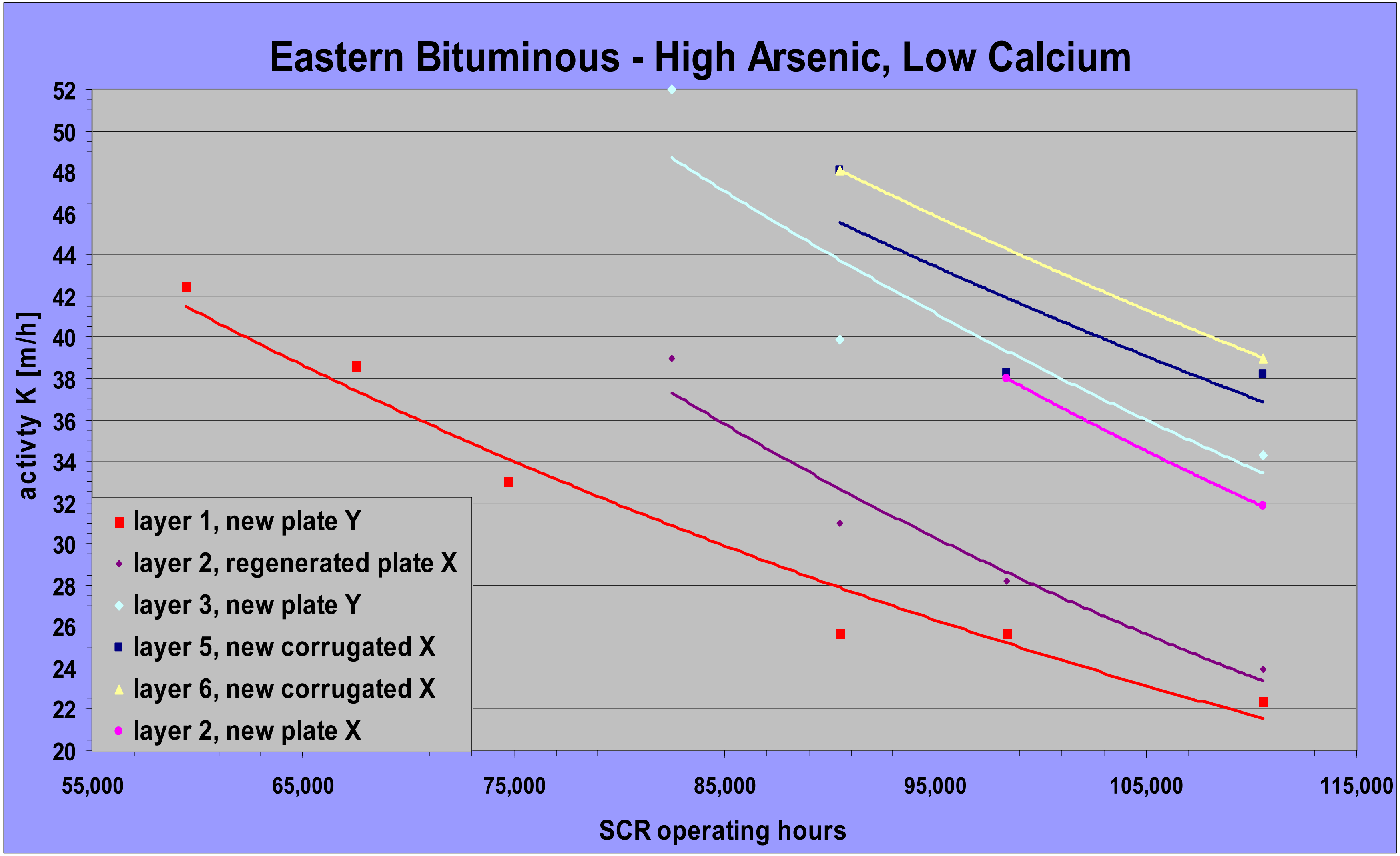
Database for Actual Deactivation



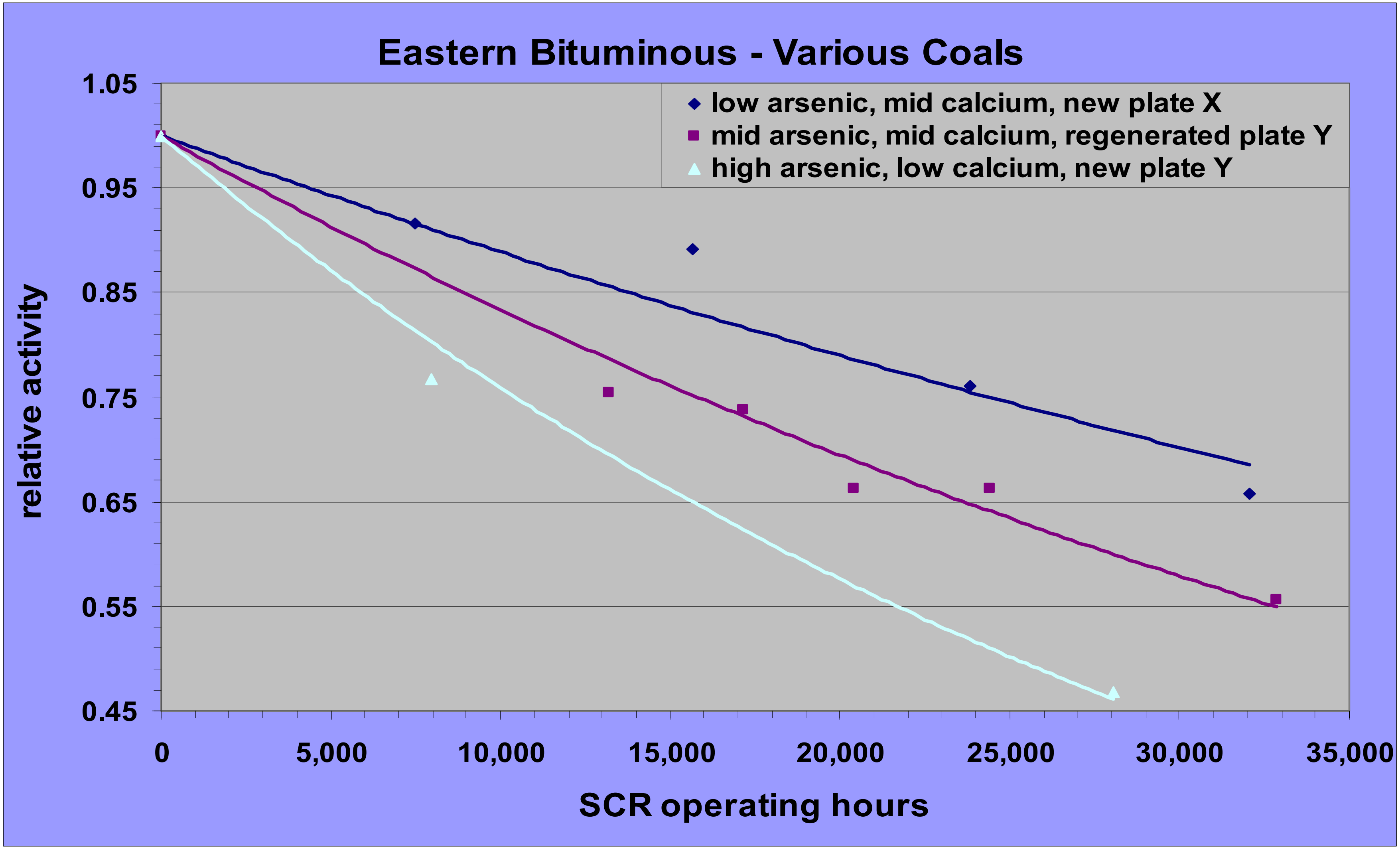
Database for Actual Deactivation



Database for Actual Deactivation



Database for Actual Deactivation



Mid Arsenic Case Study – Wansley 1

- Central and Southern Appalachian coals with mid arsenic and mid calcium contents.

- Deactivation is about what was initially expected.

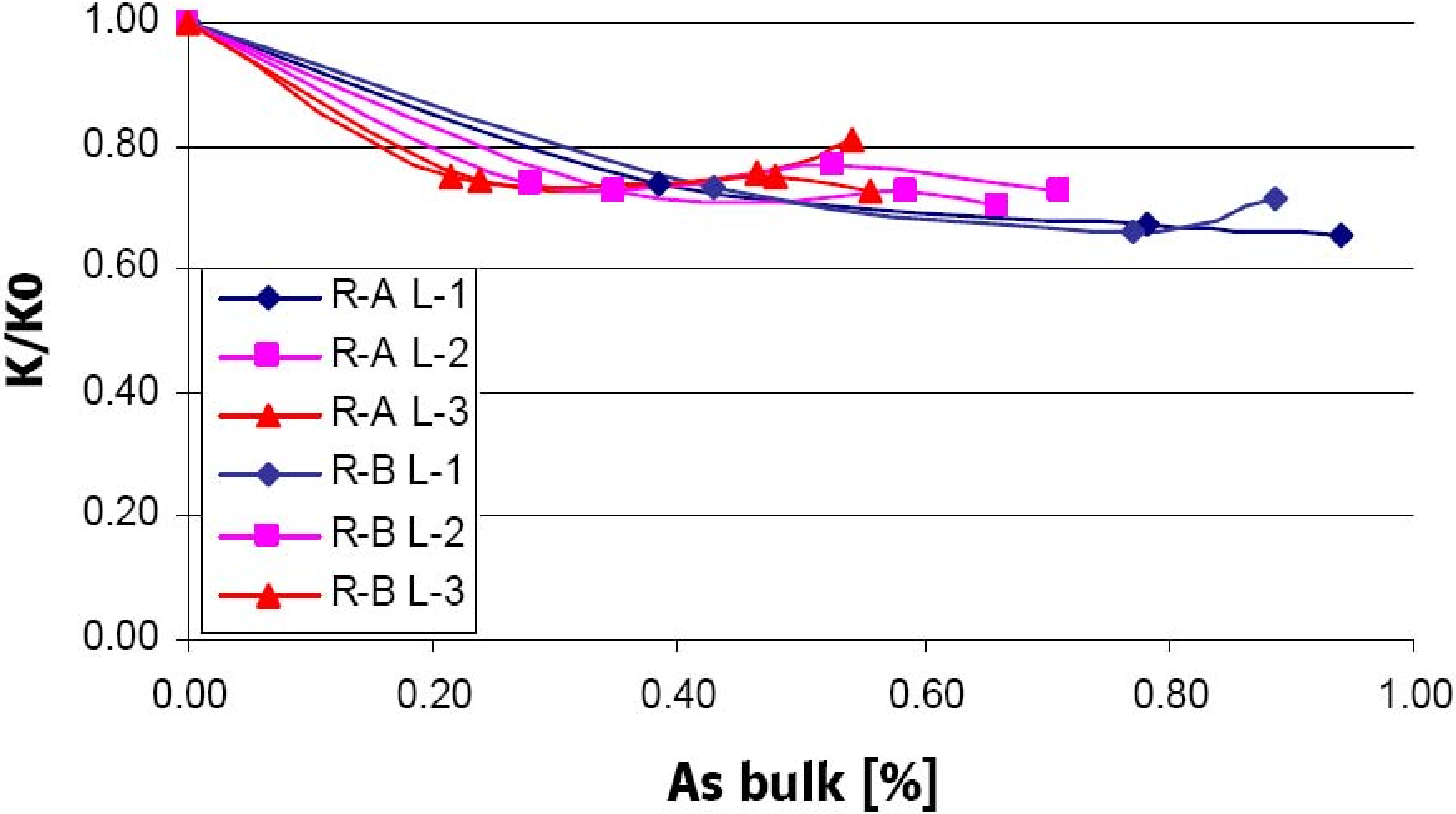
- Arsenic deactivation seems to have reached saturation as deactivation appears to have leveled out.

- Peculiarity: Inverse deactivation was noted initially, which means that the deactivation is greater on lower (downstream) layers than on higher (upstream) layers. This is unusual for bituminous coal units but is supported through data showing higher deactivation at the lower layers initially. The trend reversed to what would be considered normal now.

EVONIK INDUSTRIES

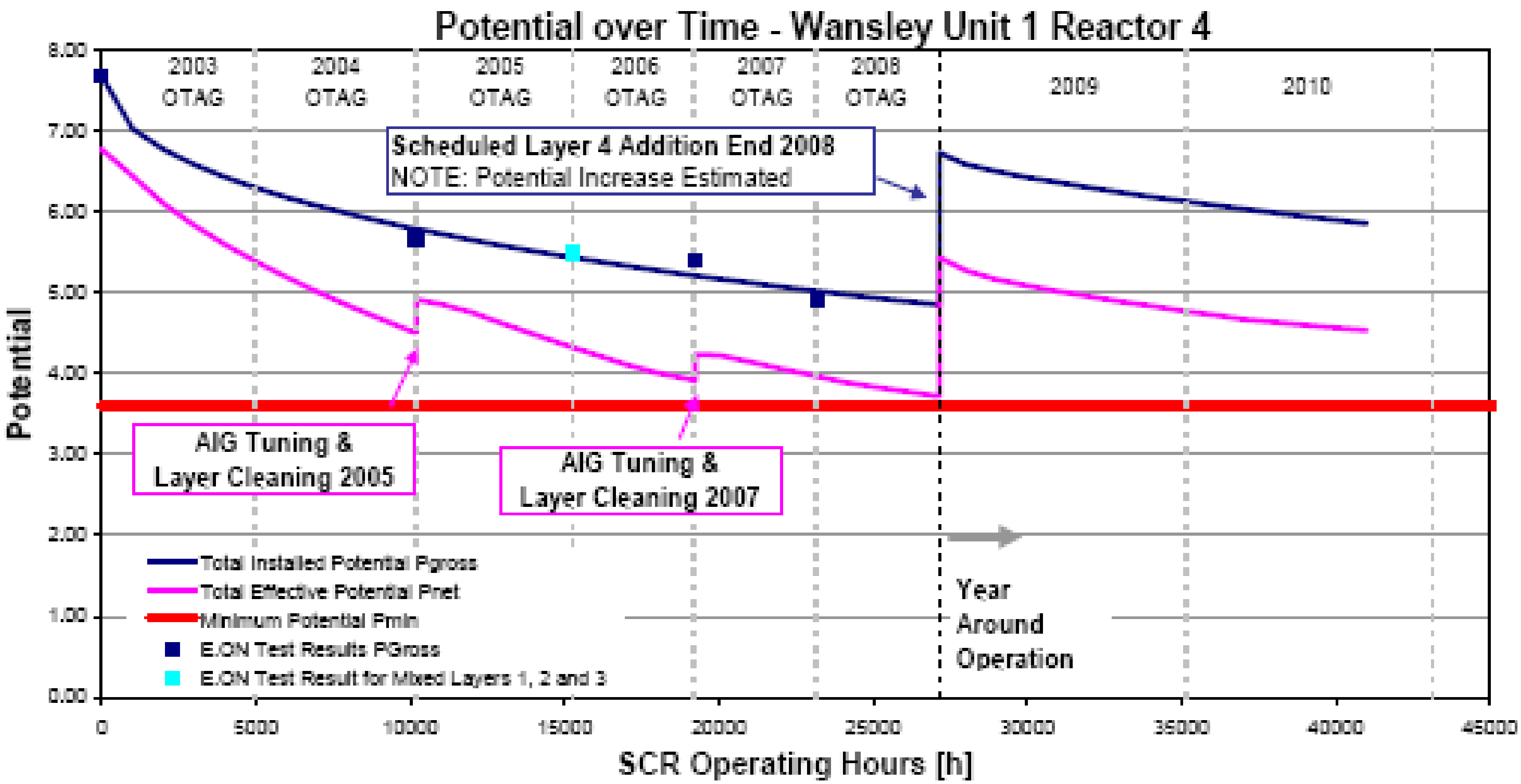
SOUTHERN COMPANY

Mid Arsenic Case Study – Wansley 1



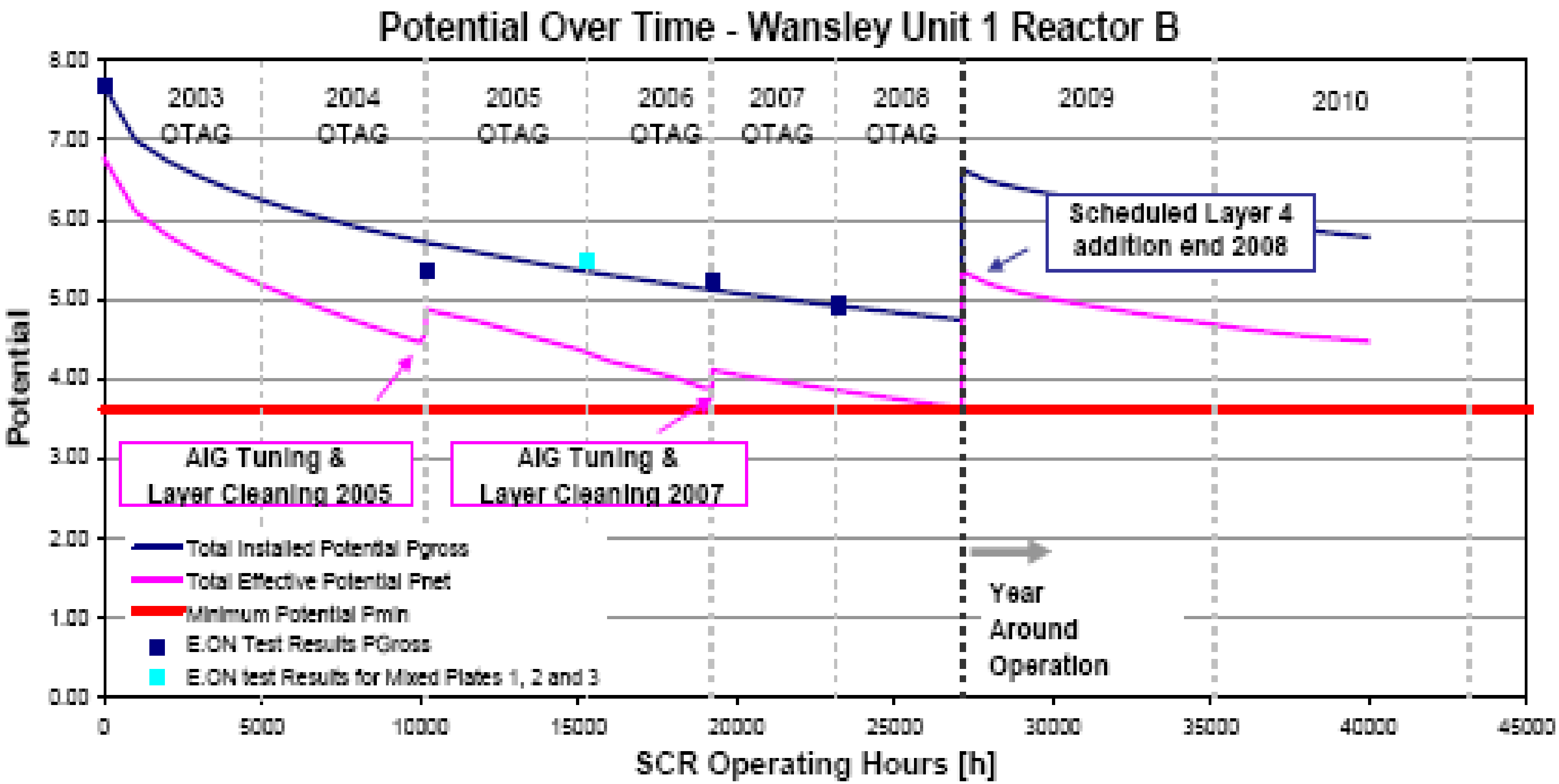
Mid Arsenic Case Study – Wansley 1

Figure 3 a: DeNOx Potential versus Operation Time - Wansley Unit 1 Reactor A

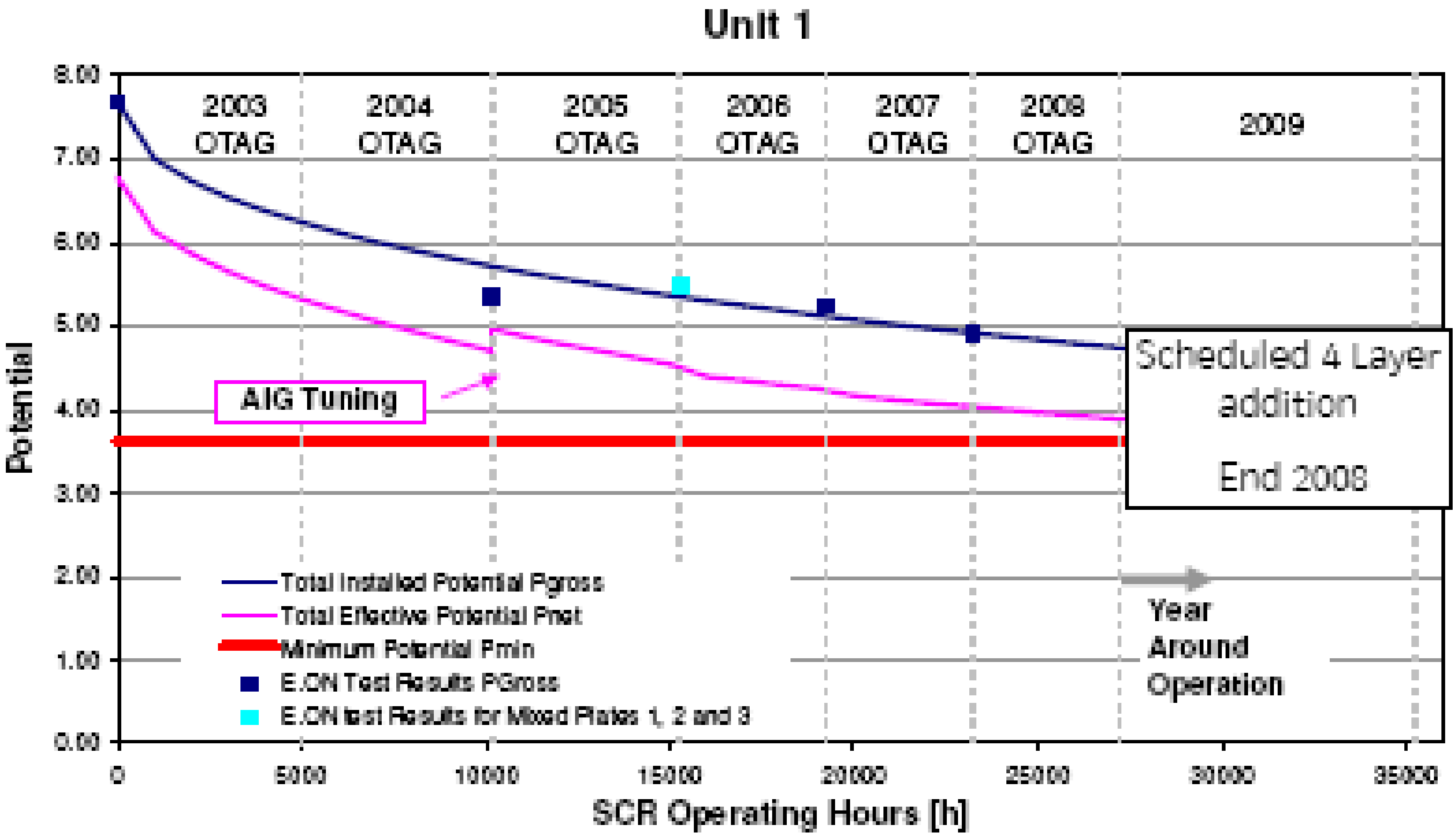


Mid Arsenic Case Study – Wansley 1

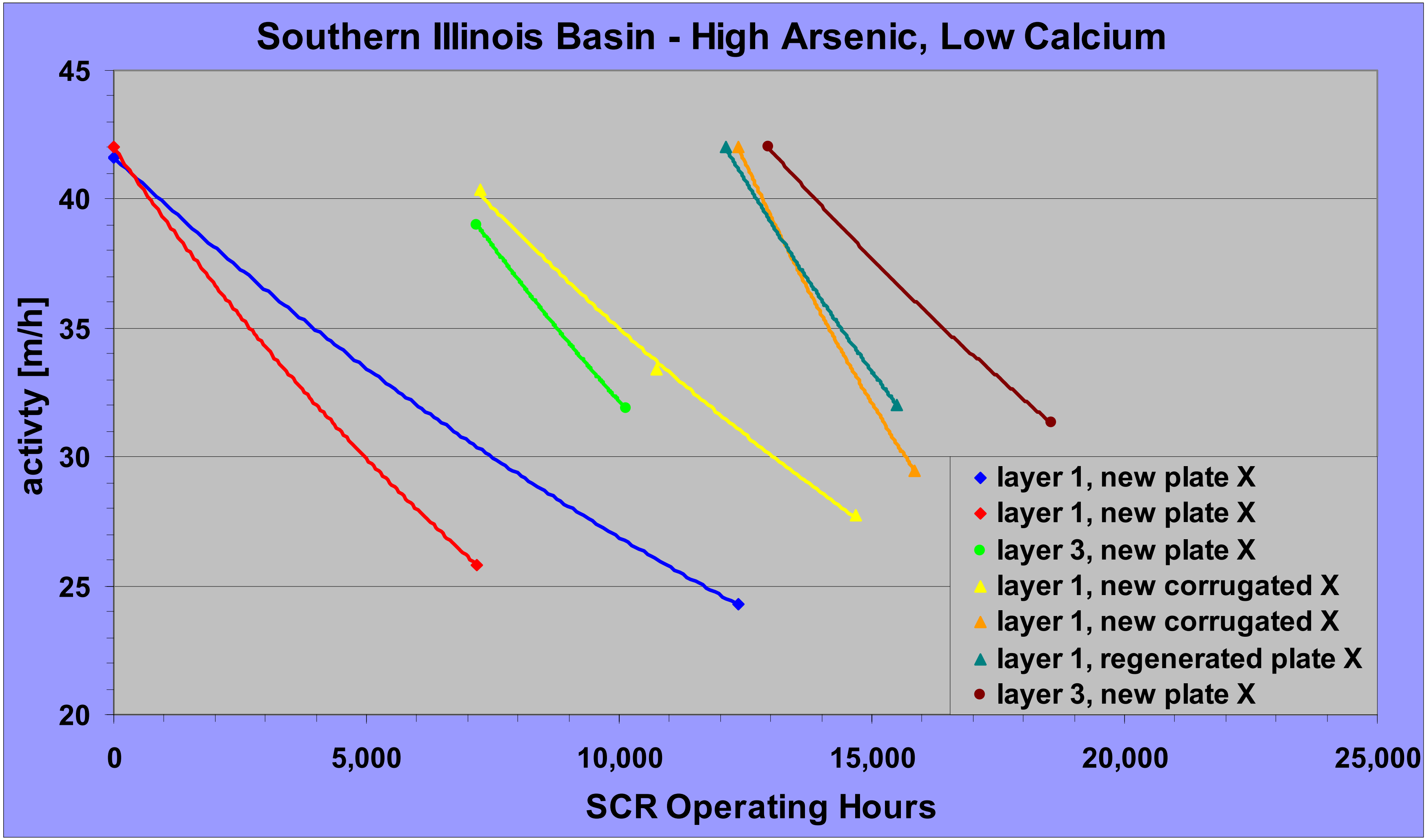
Figure 3 b: DeNOx Potential versus Operation Time, Wansley Unit 1 Reactor B



Mid Arsenic Case Study – Wansley 1



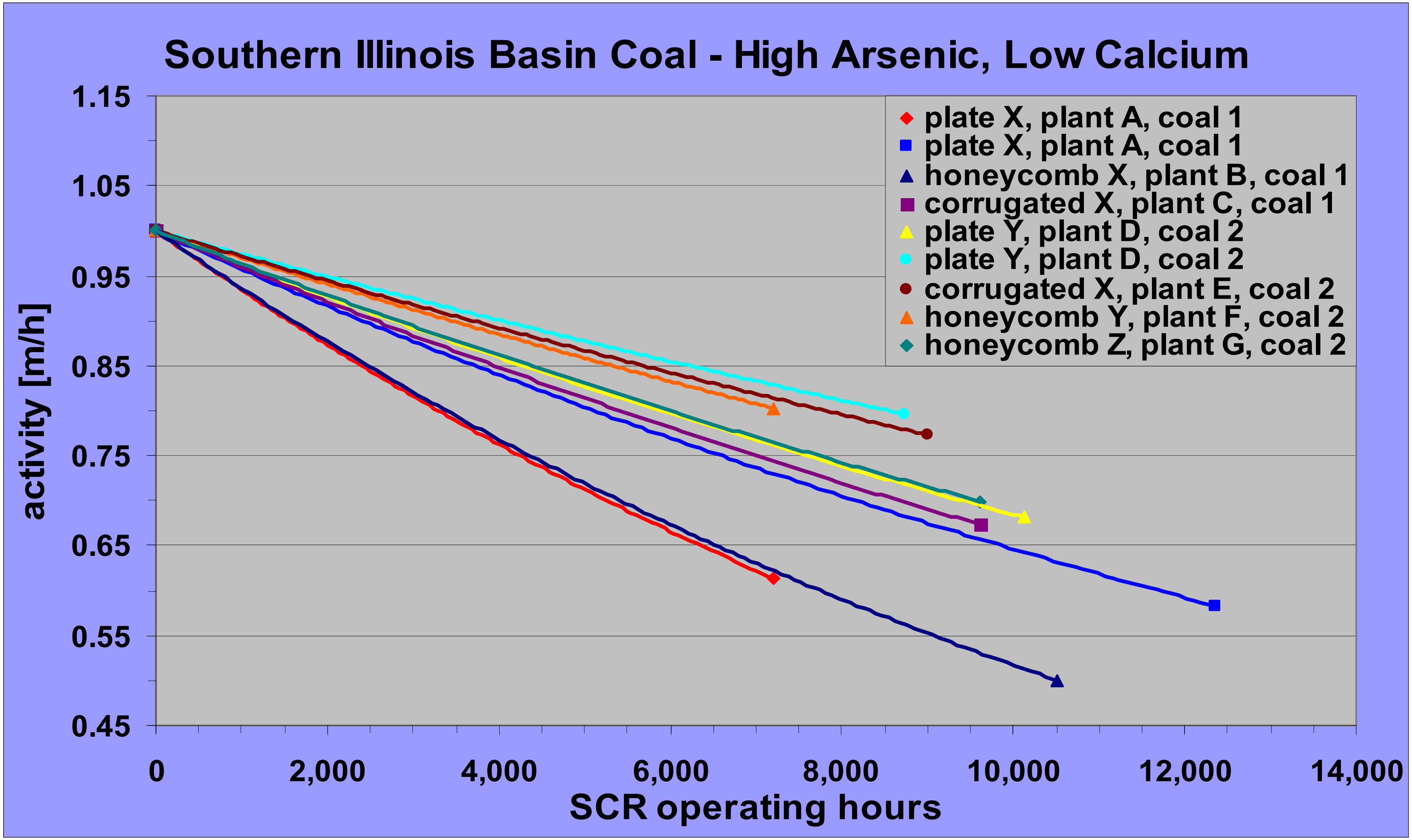
Database for Actual Deactivation



EVONIK INDUSTRIES

SOUTHERN COMPANY

Database for Actual Deactivation



EVONIK INDUSTRIES

SOUTHERN COMPANY

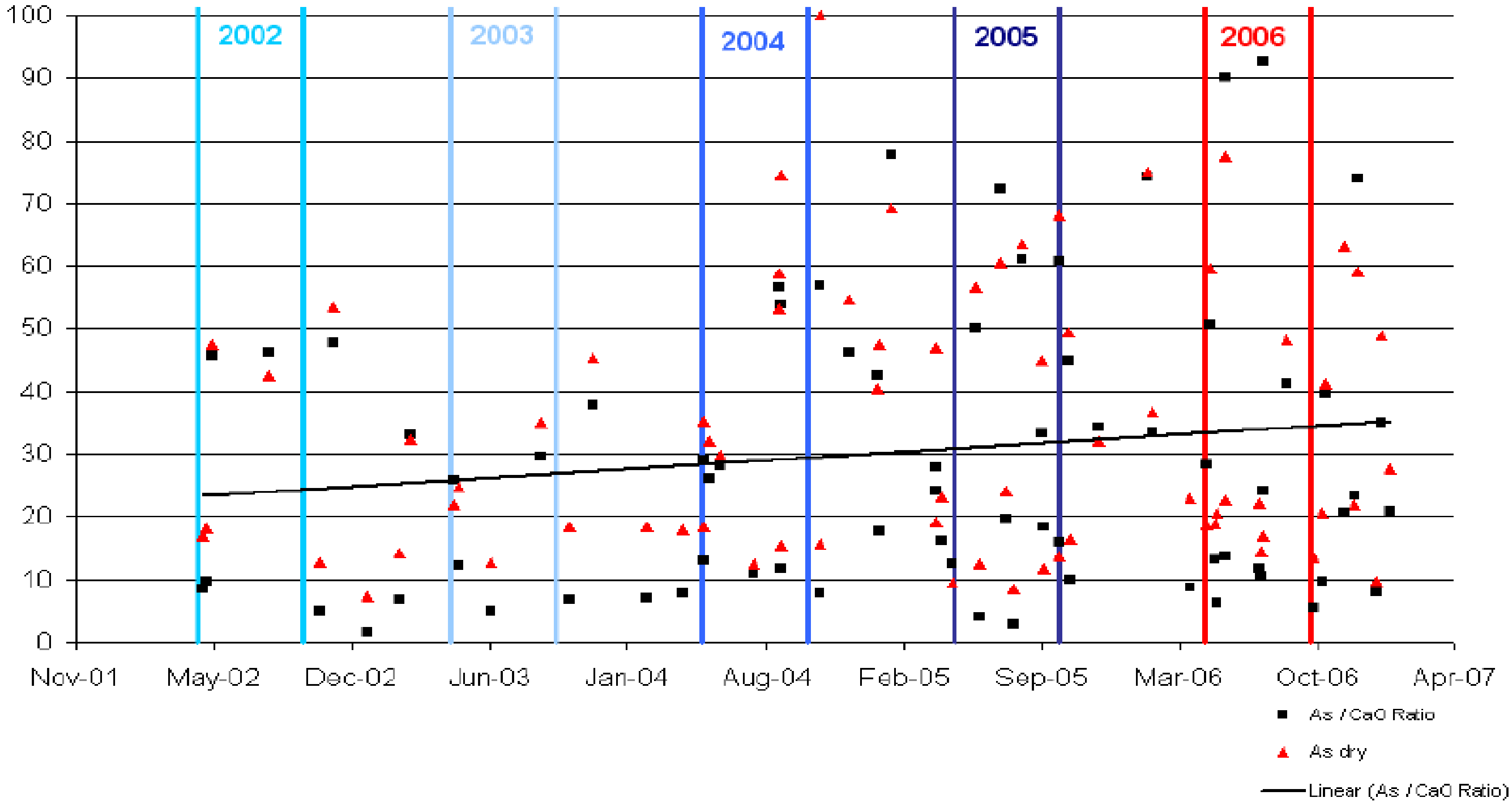
High Arsenic Case Study – Gorgas 10

- **Important trends in Northern Alabama coal burned:**
  - **Increasing variability of the As/Ca ratio.**
  - **Increase in absolute arsenic concentration.**
  - **Deacrease in heating value and increase in ash content.**

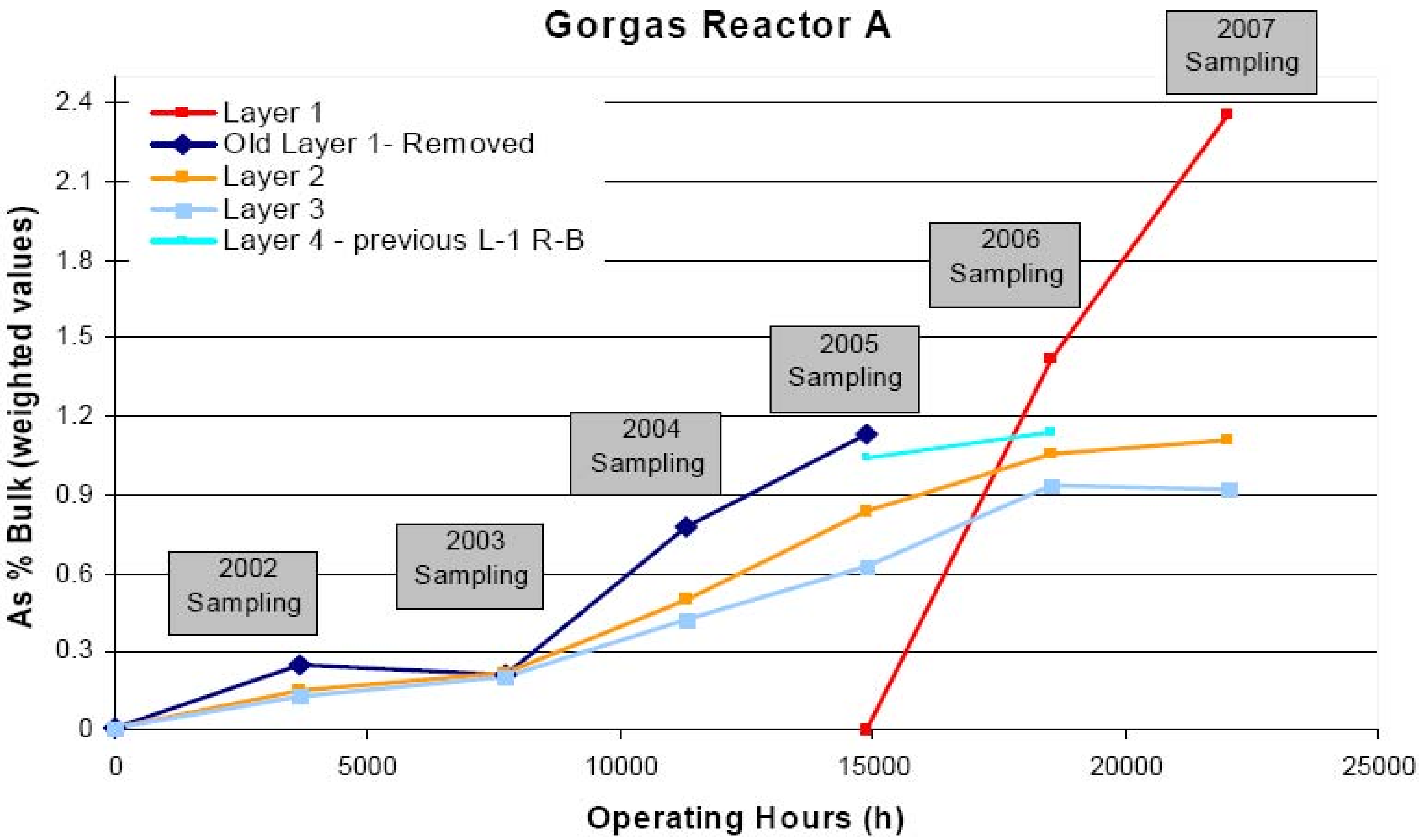
- **Observations:**
  - **Plate catalyst shows a greater and/or quicker uptake of arsenic update than honeycomb (same as in Europe).**
  - **Arsenic uptake appears to reach saturation since K/K_0 is now about the same on all layers regardless of catalyst type and make (same as in Europe).**
  - **SEM shows arsenic gradient across wall of catalyst with higher [As] on walls and lower in the middle regardless of catalyst type and make (same as in Europe).**

High Arsenic Case Study – Gorgas 10

Figure 1: Gorgas Unit 10 Fuel Analyses (Data provided by Southern Company)



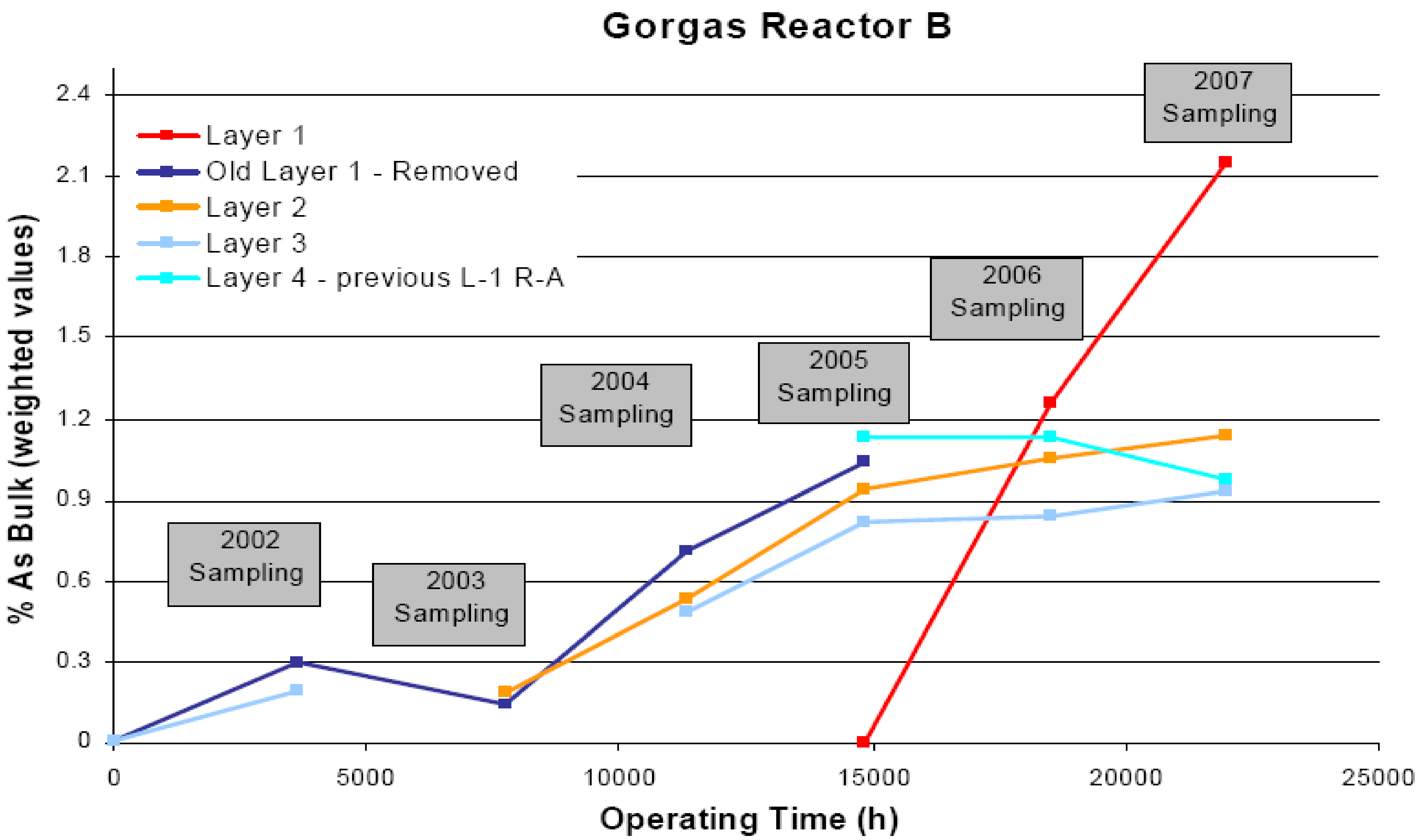
High Arsenic Case Study – Gorgas 10



EVONIK INDUSTRIES

SOUTHERN COMPANY

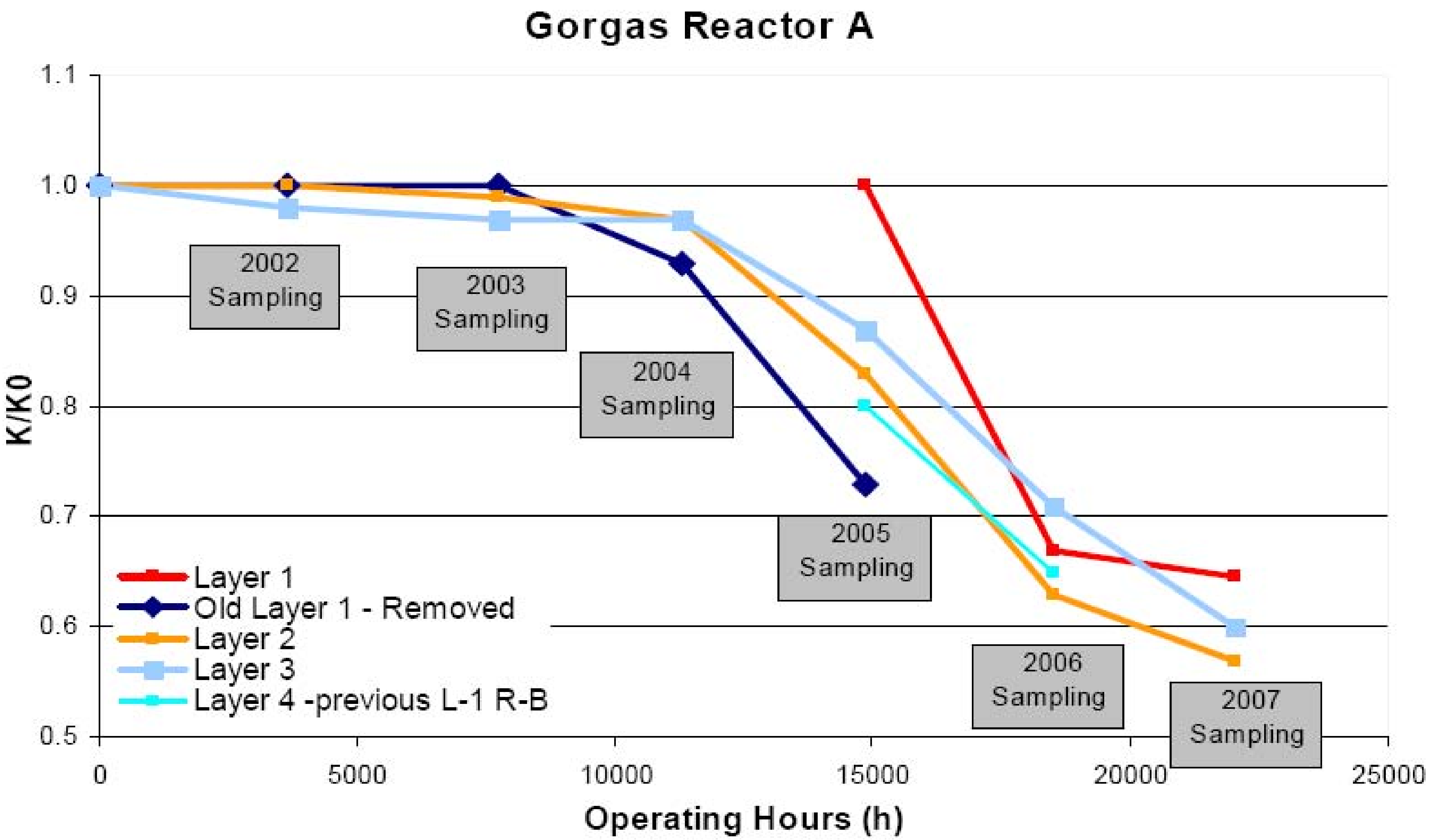
High Arsenic Case Study – Gorgas 10



EVONIK INDUSTRIES

SOUTHERN COMPANY

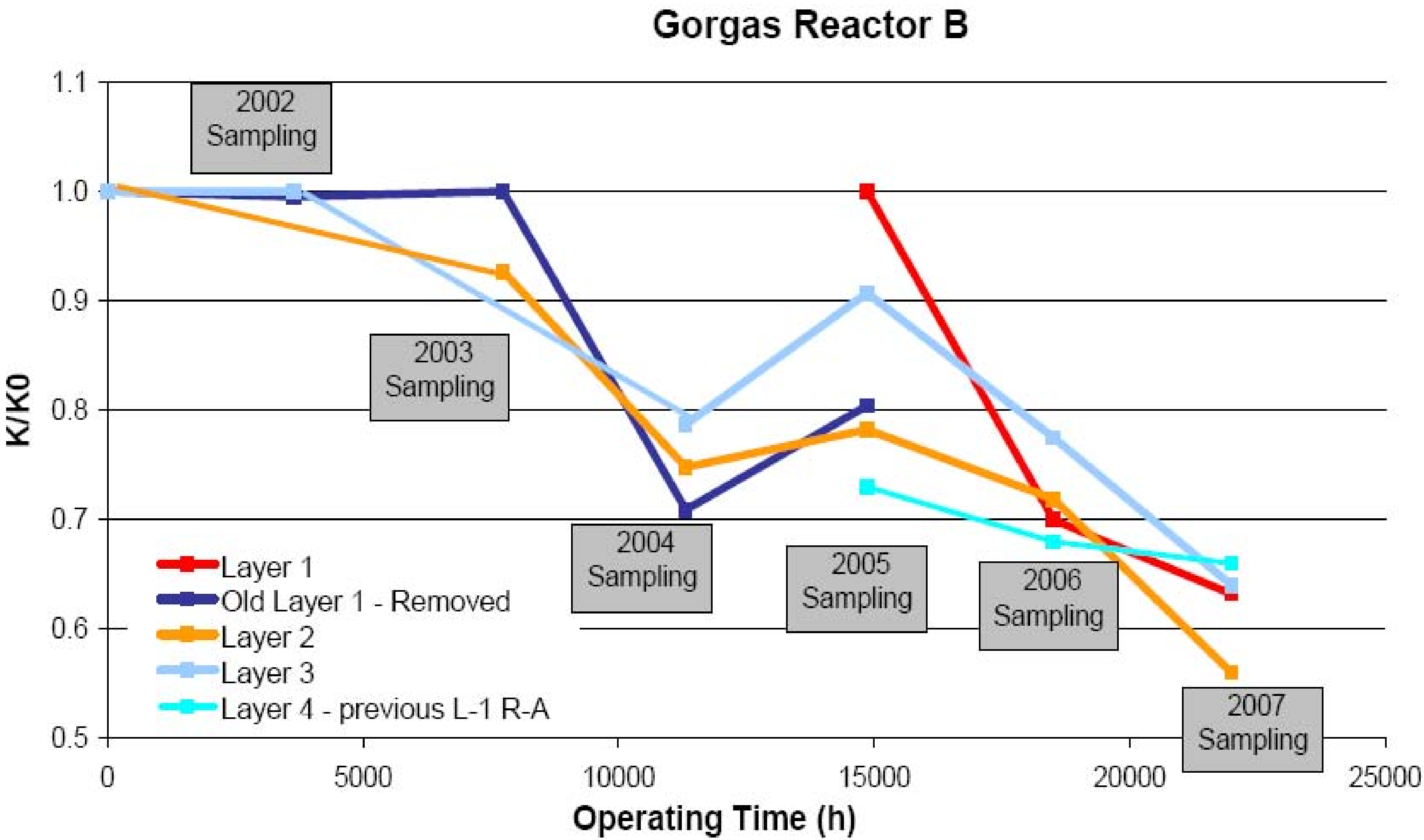
High Arsenic Case Study – Gorgas 10



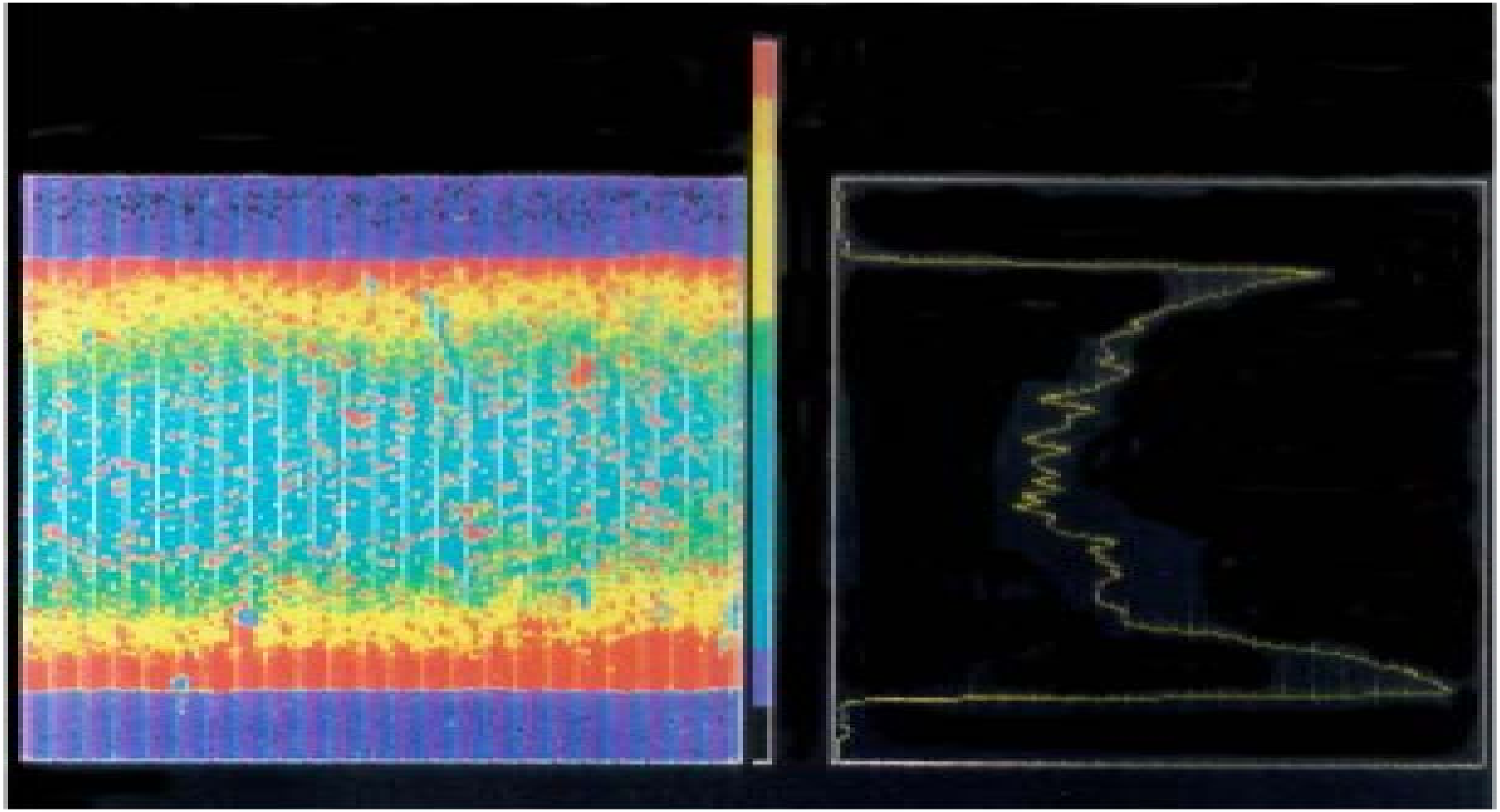
EVONIK INDUSTRIES

SOUTHERN COMPANY

High Arsenic Case Study – Gorgas 10

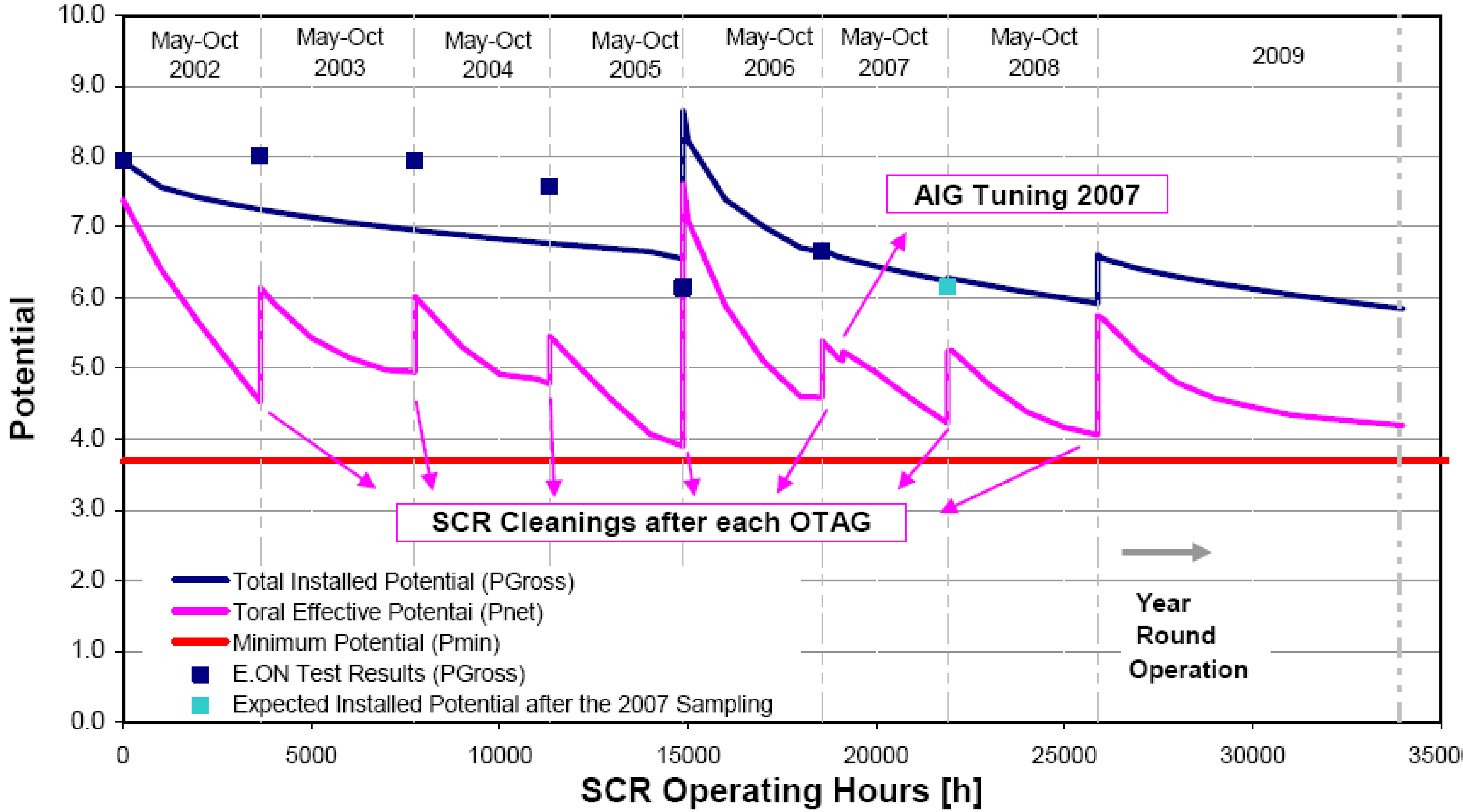


High Arsenic Case Study – Gorgas 10



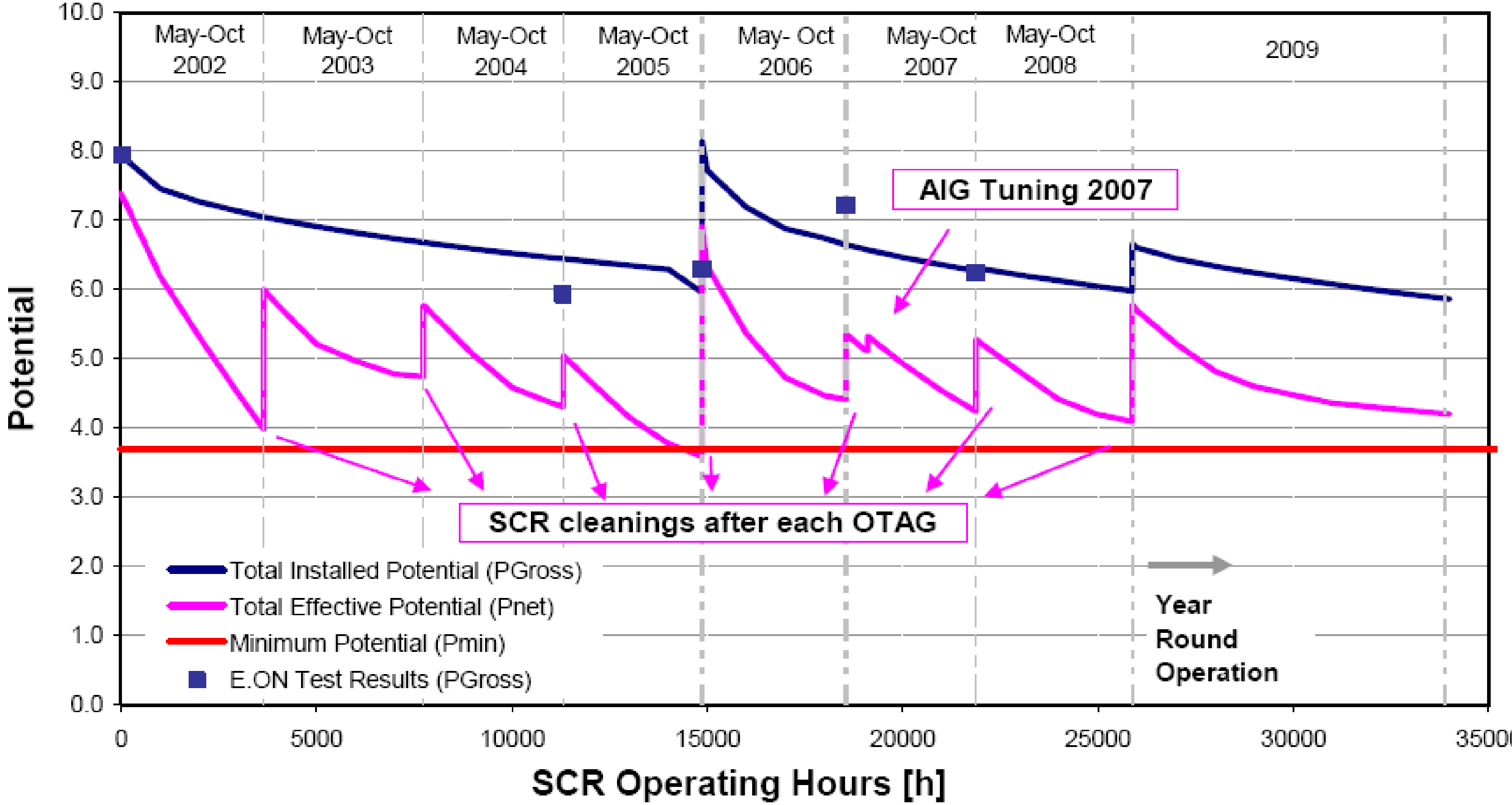
High Arsenic Case Study – Gorgas 10

Figure 5a: DeNOx Potential versus Operation Time - Reactor A



High Arsenic Case Study – Gorgas 10

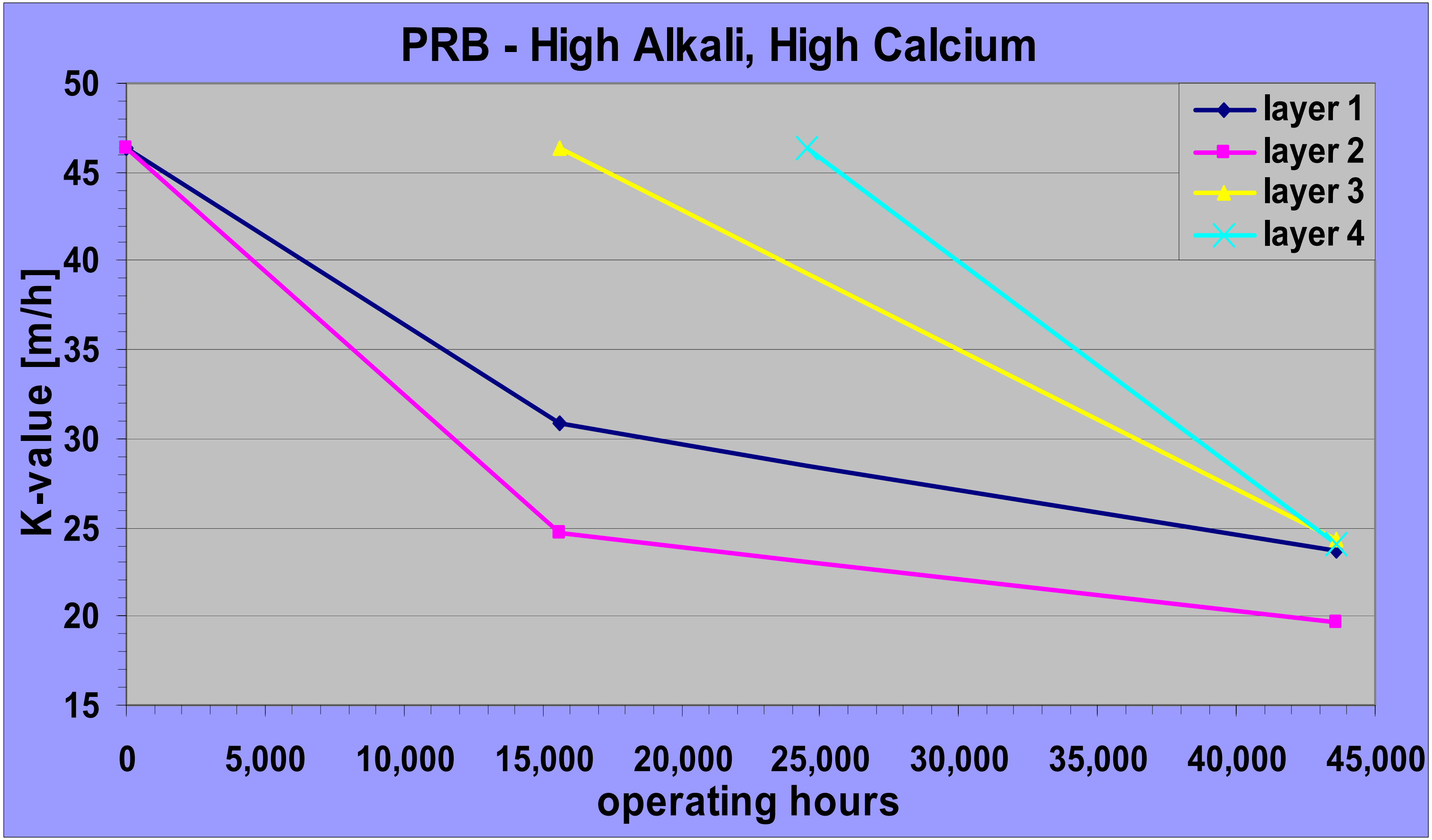
Figure 5b: DeNOx Potential versus Operation Time - Reactor B



EVONIK INDUSTRIES

SOUTHERN COMPANY

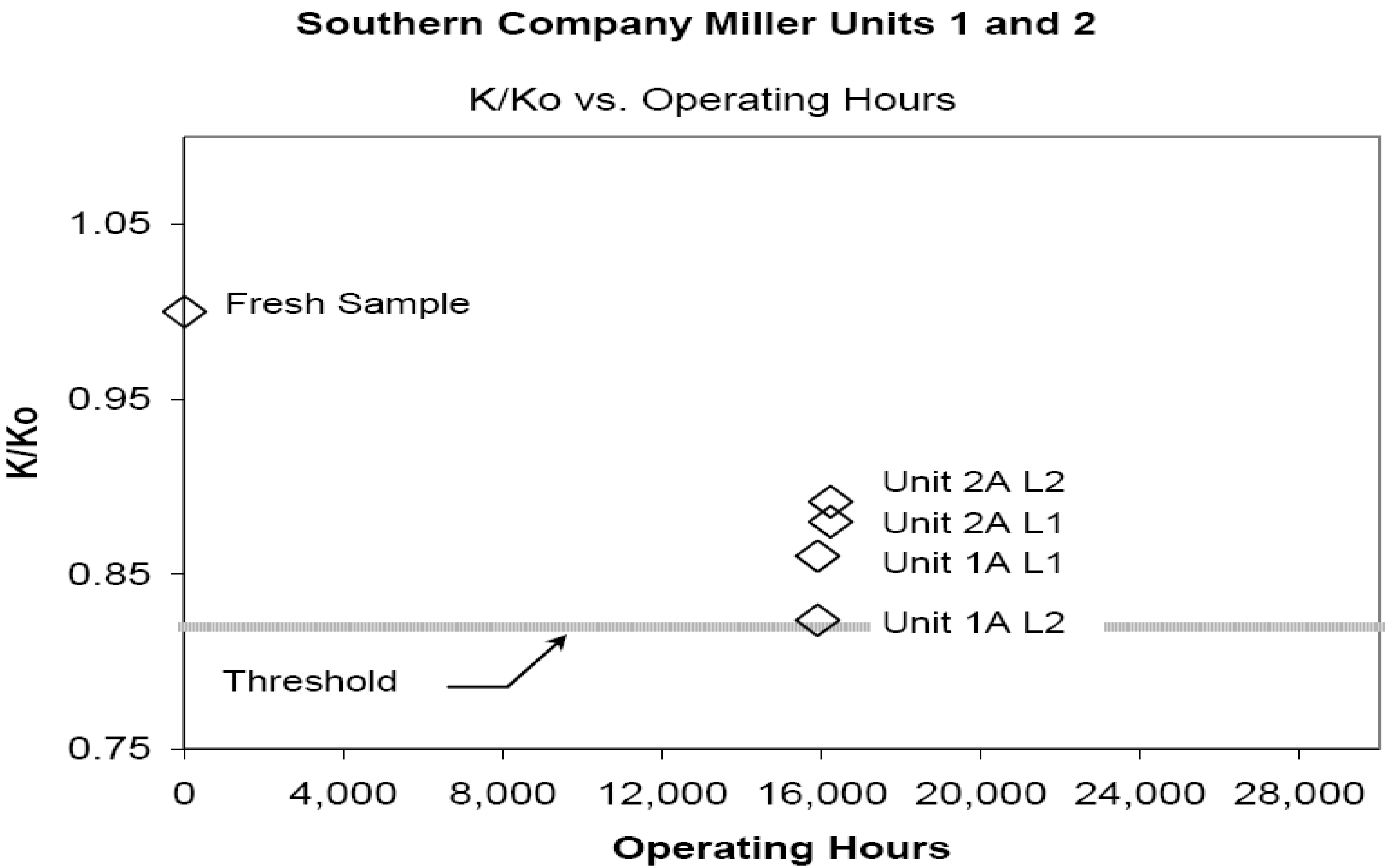
Database for Actual Deactivation



PRB Case Study – Miller 1, 2, 3 & 4

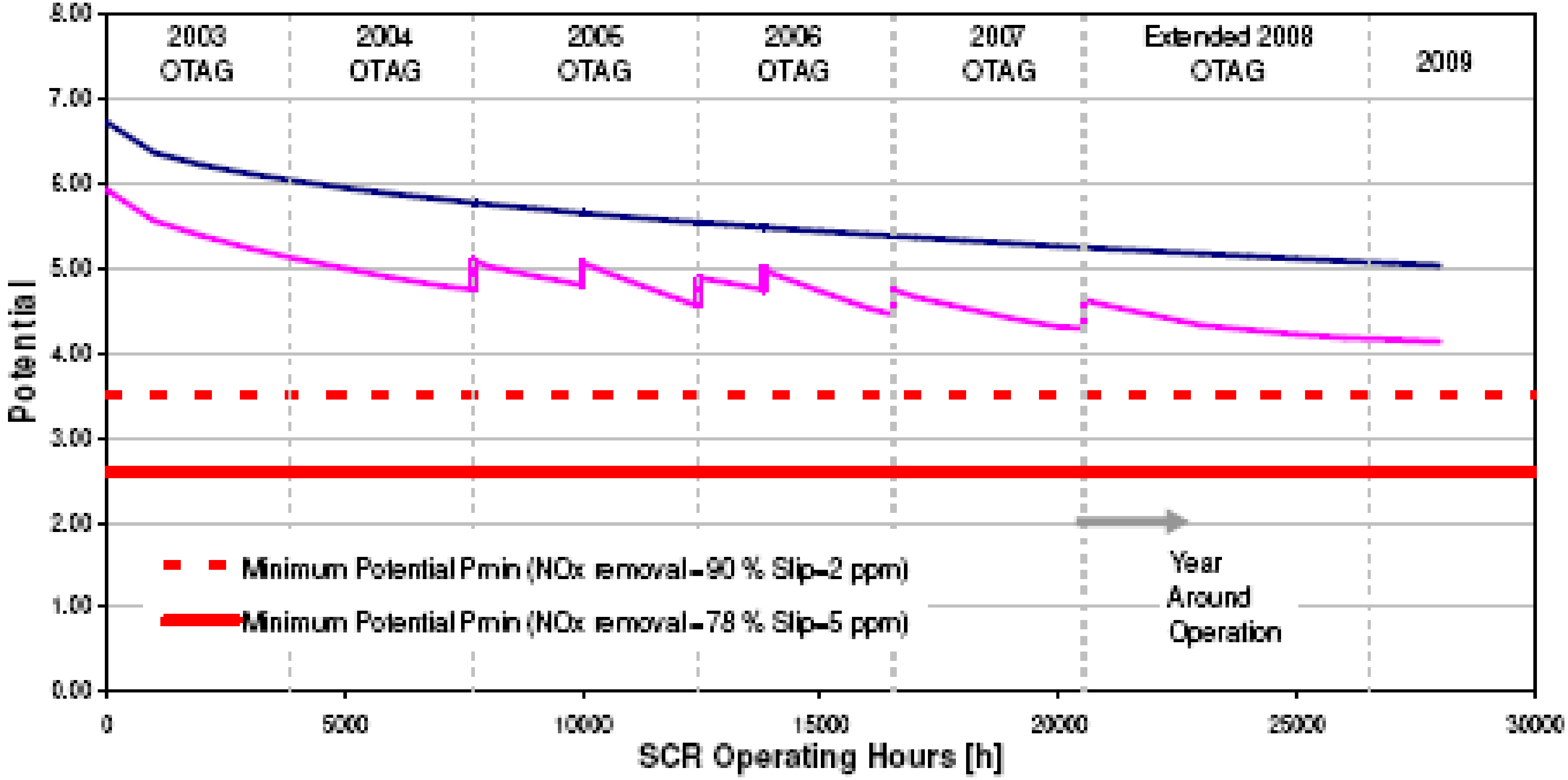
- **PRB fuel – high calcium, high alkali, high phosphorus.**
- **Deactivation significantly better than initially expected (although, Miller was designed conservatively).**
- **Deactivation due to gypsum layer deposition on surface of catalyst.**
- **Inverse deactivation noted – deactivation greater on lower layers than on higher (top) layer. This is not unusual for PRB units and has been observed elsewhere also.**
- **Also significant is gross versus effective/available DeNOx potential due to fly ash plugging. Southern Company is trending towards larger pitch whereas the industry appears to be going to smaller pitch.**

PRB Case Study – Miller 1, 2, 3 & 4



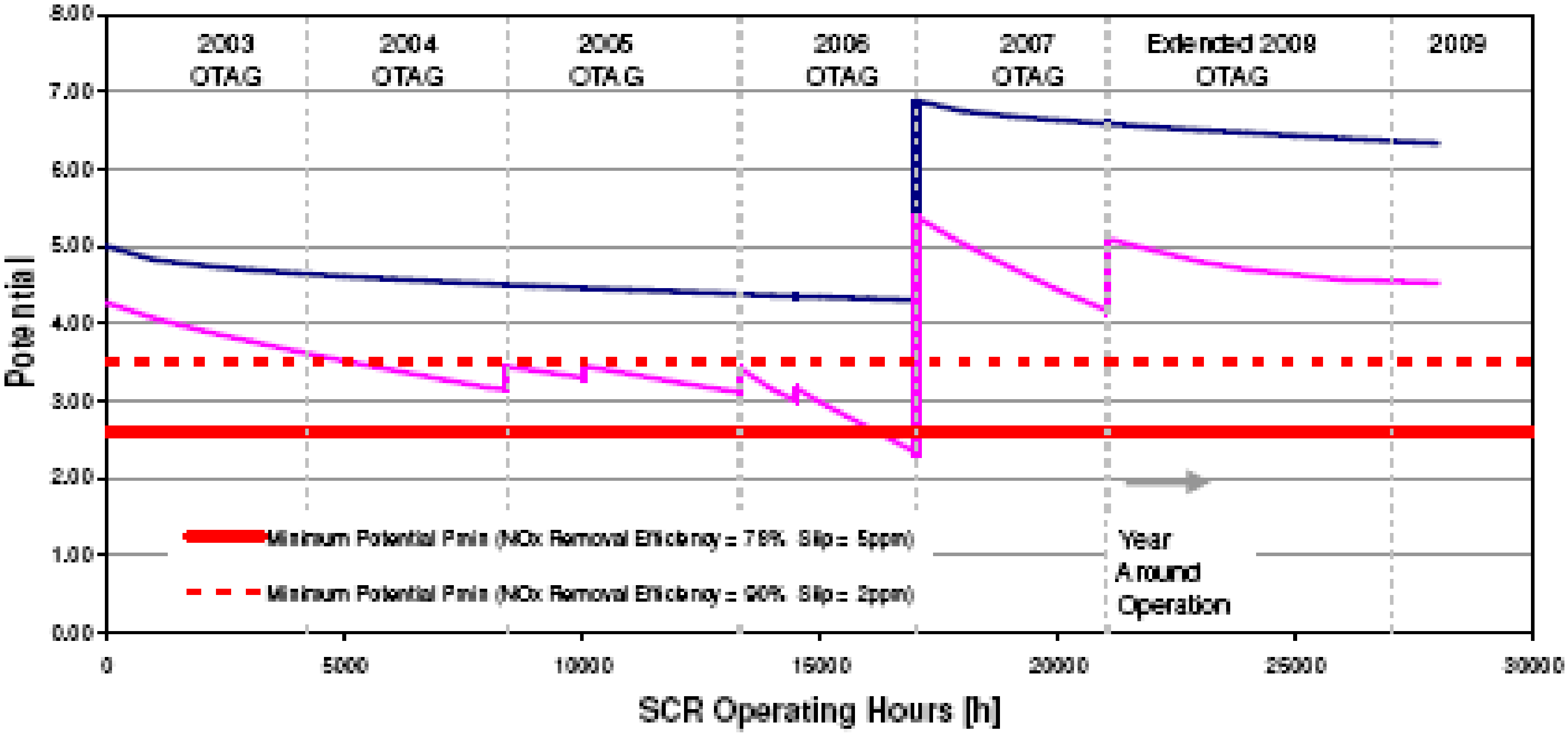
PRB Case Study – Miller 1, 2, 3 & 4

Plant Miller Unit 4 – 8.2 mm pitch



PRB Case Study – Miller 1, 2, 3 & 4

Plant Miller Unit 3 – 9.3 mm pitch



EVONIK INDUSTRIES

SOUTHERN COMPANY

Conclusions

- **Theory suggests that chemical deactivation mechanisms and deactivates rates should be essentially the same for all catalyst types and makes as they are primarily dependent on the composition of the coal burned.**

- **Actual field data confirms theory as all makes and types of catalyst deactivate chemically at essentially the same rate when exposed to the same flue gas in the same SCR reactor. This is also true for regenerated catalyst.**

- **Catalyst make and type can be selected only based on:**
  - **Suitable geometry (pitch, mechanical strength, etc.).**
  - **Lowest price per DeNOx potential unit.**

- **There is no such thing as arsenic resistant SCR catalyst.**

Questions?