APPENDIX A

"CORRECTION OF T_{cr} MEASUREMENTS FOR ASH CONTENT"

CORRECTION OF T_{cr} MEASUREMENTS FOR ASH CONTENT

The original T_{cr} measurements were done on chars from coals which originally had about 10% ash. Consequently, the chars had about 20% ash content (assuming 50% weight loss and no ash loss). In order to apply the method to coals which have significantly different ash content, a correction needs to be applied as described below.

W_o = Initial sample weight
W_a = Ash content in the sample plus moisture
W = Sample weight during sample oxidation

$\Phi = W/W_o$, $\Phi_a = W_a/W_o$

$\Phi = \Phi(T)$ and $d\Phi/dT$ are obtained from TGA experiment (balance and first derivative curves)

Let Ψ = fraction (daf) unoxidized char, then

$$\Psi = \frac{\Phi - \Phi_a}{\Phi_o - \Phi_a} = \frac{\Phi - \Phi_a}{1 - \Phi_a} = \frac{W - W_a}{W_o - W_a}$$

$$\frac{d\Psi}{dt} = \frac{(d\Phi/dt) - 0}{1 - \Phi_a} = \frac{d\Phi/dt}{1 - \Phi_a}$$

the definition of T_{cr} is $\frac{d\Phi}{dt} \equiv -0.11$ wt. fraction/min

Solving for $d\Phi/dt$:

$$\frac{d\Phi}{dt} = (1 - \Phi_a)\frac{d\Psi}{dt} = -0.11\ \text{min}^{-1}$$

$$\text{or } \frac{d\Phi}{dT} \cdot \frac{dT}{dt} = -0.11\ \text{min}^{-1}$$

$$\text{but } \frac{dT}{dt} = 30°\text{C/min}$$

S87 14th Tables 5/90

$$\therefore \frac{d\Phi}{dT} = -0.11/30\ ^\circ C^{-1}$$

$$= -3.67 \times 10^{-3}\ ^\circ C^{-1}$$

or T_{cr} = T where $d\Phi/dT = -3.67 \times 10^{-3}\ ^\circ C^{-1}$

When $\Phi_a = 0$, $d\Phi/dT = d\Psi/dT$

For the previous chars, the value of Φ_a was - 0.2. Consequently, in order to convert to an ash free basis:

$$\frac{d\Psi}{dT} = \frac{1}{(1-\Phi_a)} \frac{d\Phi}{dt}$$

$$= \frac{1}{(1-0.2)} 3.67 \times 10^{-3} {}^\circ C^{-1}$$

$$= 4.6 \times 10^{-3} {}^\circ C^{-1} \text{ (ash free)}$$

In order to obtain T_{cr} measurements on higher or lower ash chars, the number of units on the derivative curve must be modified accordingly. For example, if the original measurement was $d\Phi/dT$ = 3 units for Φ_a = 0.2, then a char with X% ash would adjust the numbers of units as follows (for the equivalent $d\Psi/dT$)

$$\frac{3 \text{ units}}{(1-0.2)} = \frac{n \text{ units}}{(1-X)}$$

if X = 0.1, n = 3.4 units
if X = 0.5, n = 1.9 units

Additional Note

Because of a difference in the scale factors in our TGA for the balance curves versus the derivative curves, the value of $d\Phi/dt$ used for our T_{cr} measurements was actually .06 wt. fraction per minute rather than 0.11 wt. fraction per minute. For a typical char (with a 20% ash content), the difference in T_{cr} by these different criteria is about 25°C.