HITECH INSTRUMENTS **Technical Note**

The Use of Zirconia Oxygen Analysers in Heat Treatment

Zirconia Oxygen analysers can be used to measure the properties of a heat treatment atmosphere (carburising, annealing etc.) by measuring the amount of oxygen in them.

In a carburising furnace, a hydrocarbon, typically natural gas or propane, is "cracked" to provide the atmosphere. The "cracking" is really burning with too little oxygen, so that not all the carbon and hydrogen in the fuel gas is used up. The equations below illustrate this, using methane (natural gas) as fuel.

Stoichiometric combustion (stoichiometric means exactly the right amount of one chemical to react with another) looks like this:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

But if you "crack" the fuel with too little oxygen, you get this:

$$4CH_4 + 4O_2 = 2CO + 2CO_2 + 2H_2O + 6H_2$$

However, this is only one possible reaction. Depending on temperature, you could get:

$$= CO + 3CO_2 + H_2O + 7H_2$$

or even

$$= 3CO + CO_2 + 3H_2O + 5H_2$$

The other effect to be considered is dissociation, or the break-down of a molecule when heated. It is a reversible reaction and the equation must remain numerically balanced at a particular temperature. Both carbon dioxide and water will dissociate at the high temperature of our analyser, and the resulting output from the cell would be due to the oxygen from this break-down:

$$2H_2O = 2H_2 + O_2 \ldots\ldots \quad (i)$$

$$2CO_2 = 2CO + O_2 \ldots\ldots \quad (ii)$$

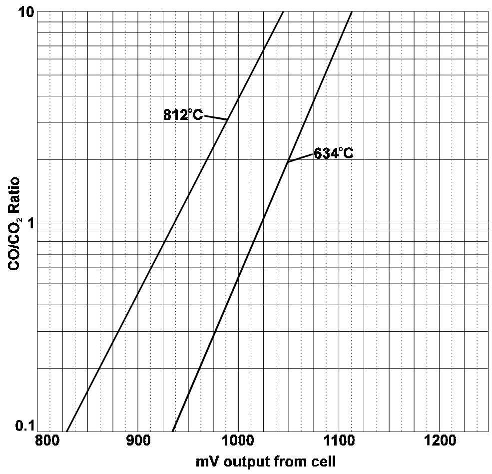
Both water and carbon dioxide dissociate equally at one particular temperature, 812°C. Since the equations must remain numerically balanced at a given temperature - if you increase the amount of (say) carbon monoxide in equation (ii), some of the oxygen will be used up to convert it to carbon dioxide. So the amount of oxygen present measures the ratio between carbon dioxide and carbon monoxide, and between water and hydrogen, which are both the same at 812°C. Oxygen is proportional to H_2O/H_2 and CO_2/CO

The general formula for the cell output at 812°C is:-

$$O/P\ (mV) = 950 - 107.7 \log \frac{OXIDES}{FUELS}$$

So a measure of oxygen made at 812°C will tell you the combined ratios of oxides to fuels, directly. At any other temperature, you also need to know the carbon/hydrogen ratio of fuel.

Referring back at the three equations for excess methane and oxygen. If you count up the molecules of oxide gases and divide by the molecules of fuel gases, you will find that the ratio is 1:2 in all cases. So it does not matter just how the methane is cracked - with a particular amount of oxygen, we will always finish up with the same ratio of oxides to fuels.



The significance of this ratio is that it determines how much carbursing potential a gas has. But the water and hydrogen play their parts too, because too much water will provide some oxygen that will combine with the carbon monoxide to form carbon dioxide, and it is the carbon monoxide that does the carburising.

So now our single measurement can replace three "traditional" measurements; those of carbon monoxide, carbon dioxide and dewpoint. Our single oxides - to - fuels measurement tells the user all he needs to know - but he may feel that he cannot interpret it in the terms that he is accustomed to.

for practical purposes, we can ignore the hydrogen/water break-down, and concentrate on the carbon monoxide/carbon dioxide. The graph shows cell output against carbon monoxide/carbon dioxide ratio. this is plotted at 634°C and 812°C, these being the two principal temperatures that our analysers are operated at, although for metallurgical processes 812°C is the more usual. We find however that more often than not the user "calibrates" our analyser output against good quality products and no longer relies on the traditional interpretation of carbon monoxide or carbon dioxide. All the user has to remember is that the higher the analyser output, the more carbon monoxide and hydrogen he has - the lower the output the carbon dioxide and water.

Zirconia analysers can be scaled to readout in kilocalories (oxygen potential) or oxide to fuel ratio. There is also an empirical approach. Read out in millivolts, and establish upper and lower readings by reference to product quality. The furnace operator simply keeps the analyser reading within those limits. For automatic operation, we can supply adjustable limit switches to do the same thing.

Other Hitech Technical Notes

TN01 "Oxygen Sensors - Theory and Application"

TN02 "Using Zirconia Oxygen Analysers to Measure the Dewpoint of Furnace Atmospheres"

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