UDC 543.27

DIRECT INSERTION TYPE ZIRCONIA OXYGEN ANALYZER HYGROMETER

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1 INTRODUCTION

Zirconia (ZrO_2) ceramic sintered by adding a slight yttria (Y_2O_3) becomes a solid electrolyte having oxygen ion conductivity at a temperature above 500 °C. A solid electrolyte plate coated with porous platinum at both surfaces acts as an oxygen sensor, and depending on the concentration of oxygen in the atmosphere in contact with both platinum electrodes, electromotive force E expressed by the following equation is generated.

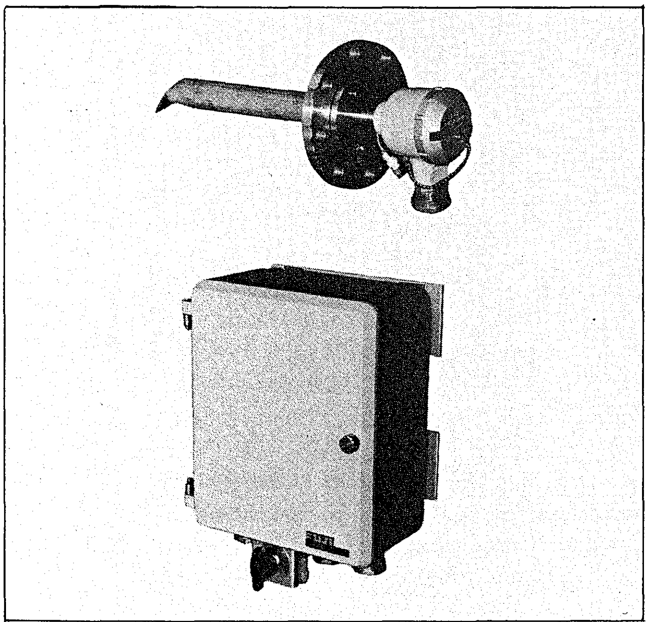
$$E = \frac{RT}{4F} \, ln \, \frac{P_1}{P_2} \quad \cdots\cdots\cdots\cdots \quad (1)$$

where, R : Gas constant
F : Faraday constant
T : Temperature of electrodes (°K)
P_1, P_2 : Concentrations of oxygen in the atmospher in contact with both electrodes

Hence, when the concentration of oxygen contained in the air (20.6 vol%) is expressed as P_1, the unknown concentration of oxygen P_2 can be obtained by measuring electromotive force E. For example, when a sensor element is heated up to 820 °C and P_1 and P_2 are respectively 20.6 vol% and 2 vol%, voltage signal of about 54 mV can be obtained. The internal resistance of this signal is normally several hundred ohms or less, and thus, the sensor generates high quality signals. Zirconia oxygen sensor is hardly to be affected by dust and steam contained in a gas to be measured. Therefore, no conditioning is required after extructing a gas to be measured, and the sensor can be used by directly inserting into dirty gas such as exhaust gas from a boiler.

This report introduces Fuji Electric's direct insertion type zirconia oxygen analyzer developed mainly to measure oxygen in boiler exhaust gas and zirconia high temperature/hygrometer developed to measure humidity in atmosphere of various drying furnaces by applying the oxygen analyzer.

Fig. 1 Direct insertion type zirconia oxygen analyzer



2 DIRECT INSERTION TYPE ZIRCONIA OXYGEN ANALYZER (TYPE ZFK2, ZFM)

(1) This oxygen analyzer consists of a small zirconia oxygen sensor which can be directly inserted into a flue, transmitter accommodated in rain-proof case and special cable which couples the sensor and transducer. The sensor generates signals depending upon concentrations of oxygen without extracting sample gas or injecting reference air. The transmitter converts the signals sent from the sensor to signals which is proportional to the concentration of oxygen, and sends them to an indicator. A temperature regulating circuit used to drive the heater of the sensor is built-in the transmitter. Further, it is possible to add an air pump and gas switching valve for air point and zero point calibrations.
(2) *Fig. 2* shows a cross-section of the zirconia oxygen sensor. Reference air must always be kept fresh around the inside electrode of the zirconia element in a test tube shape. Air is rapidly replaced by convection because the sensor is small and highly heated. For this construction, no particular air source, pump, filter, flow meter or other attachment is required. The gas to be measured is also supplied to the vicinity of the outside electrode by convection in the similar manner as the inside electrode, and the gas replacing

Fig. 2 Cross-sectional view of zirconia oxygen sensor

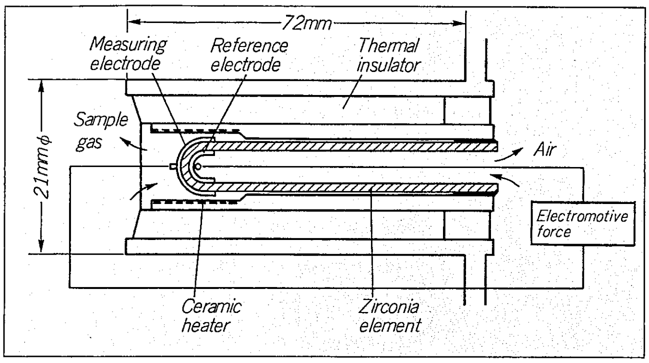


Fig. 3 Response and reproducibility data obtained by inducing air and calibration gas

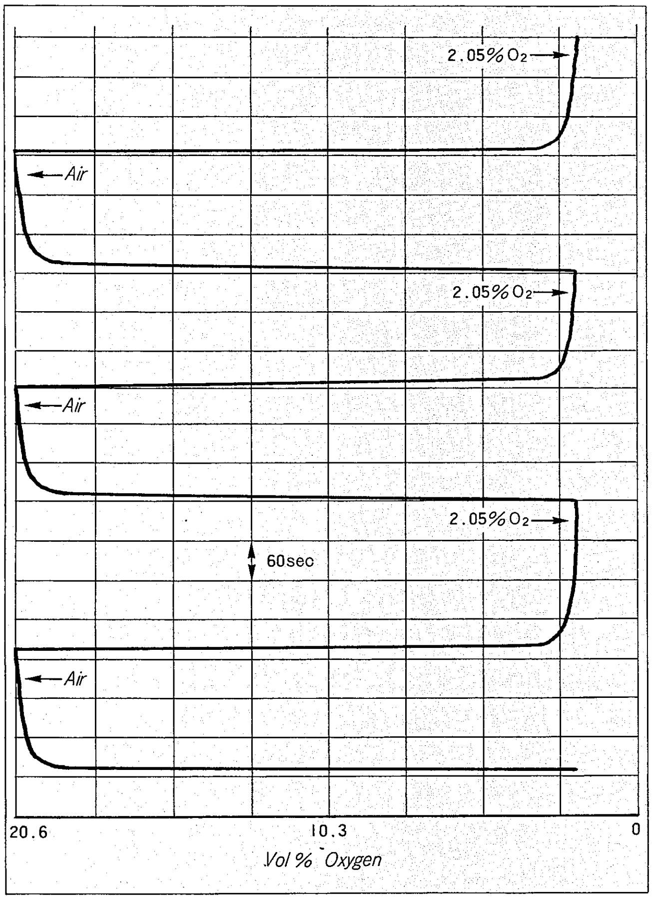


Fig. 4 Construction of flow guide tube

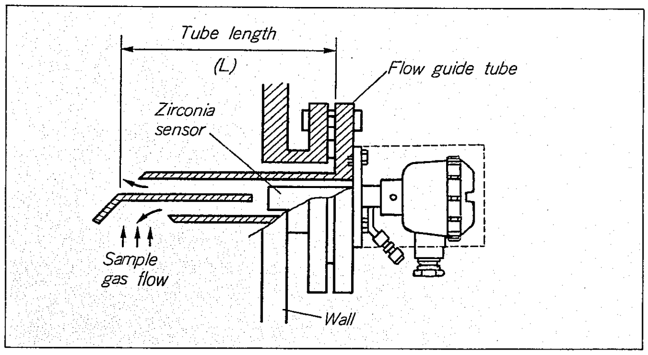
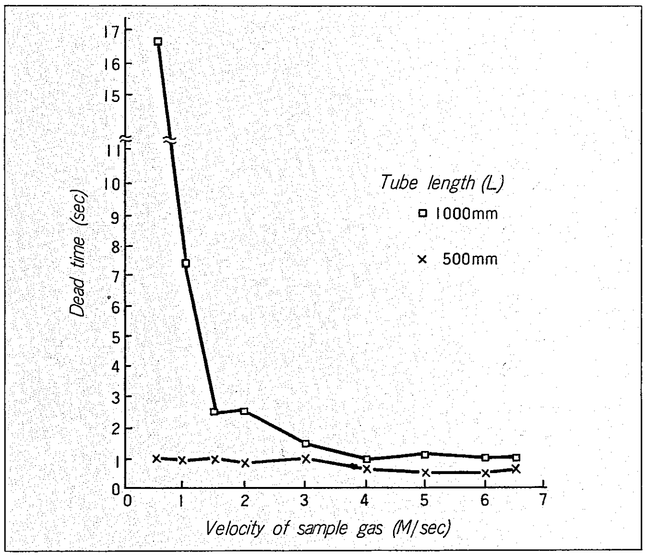


Fig. 5 Response time of zirconia oxygen analyzer with flow guide tube



speed is faster than reference air replacing speed. *Fig. 3* shows response and reproducing characteristics observed when air and zero gas are alternately introduced from the calibration gas inlet.

(3) Oxygen measurement of boiler exhaust gas is normally conducted on the gas in the center of the flue. To compensate the shortness of sensor length, a flow guide tube is used. As shown in *Fig. 4*, the flow guide tube uses gas flow energy and circulates the sample gas from a remote position to the sensor. Utilizing the flow guide tube, the sensor can be applied to flues of various sizes easily without changing the inserting length of the sensor itself. *Fig. 5* shows sample gas circulation flow speed of the flow guide tube. Normally, gas in a flue has flow velocity of about 5 meters per second or higher, and from this figure, it can be understood that the gas in the center of a flue reaches the sensor within an extremely short time.

(4) To heat the zirconia oxygen sensor up to the working temperature, a ceramic heater is used. That has a heater element buried in the ceramic. The part of this heater which comes into contact with gas is ceramic only, and therefore, the ceramic heater is not deteriorated. Further, output signals are stable because the zirconia oxygen sensor is heated evenly. *Fig. 6* shows data for long term stability of output signals of the oxygen sensor installed on a flue. In spite of dirty gas which contains high concentration of SO_2, the drift was minor and measurement was made very stably.

(5) Since the sensor is in small dimensions and heat capacity is small, maximum and mean power consumptions of the heater are respectively 70 W and about 40 W, realizing an energy saving type oxygen analyzer. Further, with the same reason, the transient property at the time of start up after turning on the power ends with such a short period

Fig. 6 Zero and span point drifts of zirconia oxygen analyzer installed on a flue (in logarithm scale)

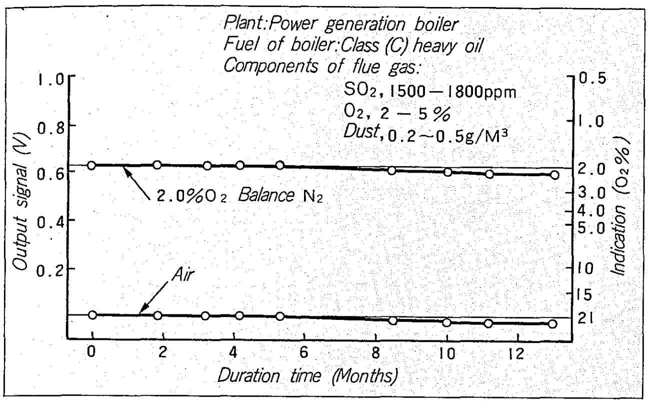


Fig. 7 Transient characteristics at the time of power on.

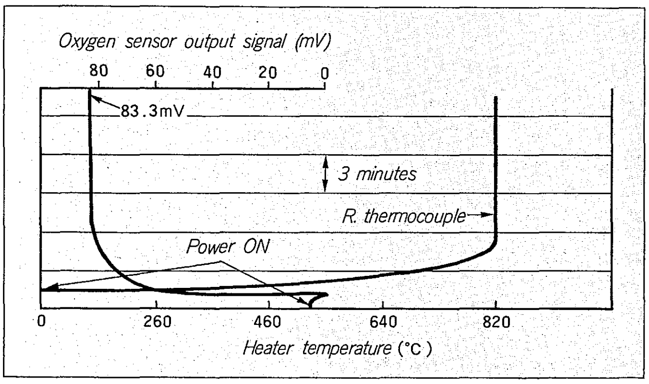
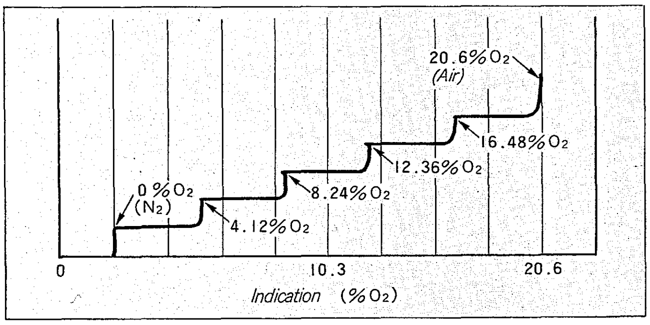


Fig. 8 Values indicated when air and nitrogen quantitatively mixed gas was measured



of time as about five minutes. *Fig. 7* shows the transient characteristic at the time of power on.

(6) Since the sensor uses a special platinum electrodes having a high activity, output impedance of the signal is low. Further, as the output characteristics are matched with the theoretical value, the linearity of the output signal converted in anti logarithm by the transmitter is excellent. To check the linearity, air and N_2 were quantitatively mixed and data was obtained by measuring the mixed gas. *Fig. 8* shows the data.

(7) General specifications

Measuring range:	0 to 5 or 0 to 10% O_2 and air point adjust range (0 to 20.6% O_2)
Reproducibility:	±0.5% of the maximum output signal
Response:	90% response 7 sec or less
Linearity:	Within ±2% of the maximum output signal
Output signal:	DC 4 to 20 mA, Linear for oxygen concentration, isolated.
Power supply:	AC 100 V, 115 V or 220 V
Power consumption:	Maximum 70 W (normally), 270 W (starting)
Weight:	Sensor . . . About 2 kg Transducer . . . About 11 kg.

(8) Applications of zirconia oxygen analyzer

Many zirconia oxygen analyzers are used to measure concentration of oxygen contained in gas exhausted from boilers which use gas and oil for the fuel, so that the combustion efficiency can be improved by adjusting air-fuel ratio. In case of a boiler which uses coal for the fuel, such a considerably large volume of dust as about 20 g/cu·m. (100 to 1000 times as great as that in case of oil) is contained in the exhaust gas. In addition, specific gravity of this dust is high. Therefore, dust is accumulated in the flow guide tube, causing gas not to be circulated. For this reason, an air supply unit and flow guide tube having an air nozzle in the tube are available. With air compressed to about 3 kg/sq·cm, accumulated dust is blown off intermittently, and thus, the oxygen analyzer can be operated for several months without conducting a maintenance service.

When the oxygen analyzer is applied to measure oxygen in an iron heating furnace, a metal flow guide tube cannot be used because flow velocity within the furnace is low and the inside is heated up to 1500 °C. For this reason, a gas ejector is available. This gas ejector consists of a gas extract tube having heat resistance up to 1600 °C and a nozzle used to circulate sample gas by the air supplied from the outside.

3 DIRECT INSERTION TYPE ZIRCONIA HYGROMETER

(1) Concentration of oxygen in completely dry air is 20.93%. When concentration of water vapor increases, concentration of oxygen decreases relatively, and when water vapor becomes 100% (for example, in a kettle in which water is boiled), concentration of oxygen becomes zero %. Consequently, concentration of water vapor in other words, humidity can be measured by measuring concentration of oxygen in the air. The following equation denotes the relationship between concentration of oxygen and concentration of water vapor.

$$0.2093\,P(H_2O) = 20.93 - P(O_2) \quad \cdots\cdots\cdots \quad (2)$$

where, $P(H_2O)$: Water vapor (Vol%)
$P(O_2)$: Oxygen (Vol%)

Only a zirconia oxygen analyzer is capable of directly

Fig. 9 Zirconia high temperature hygrometer detector

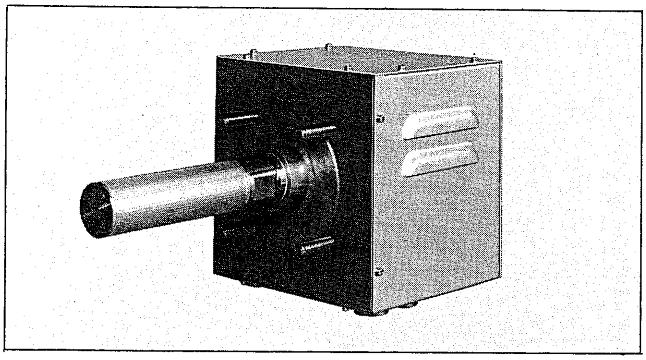
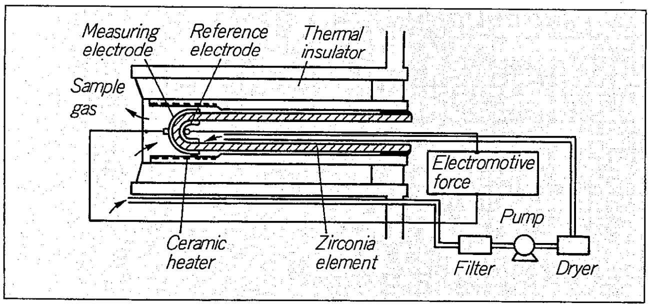


Fig. 10 Principle diagram for measuring humidity in non-air atmosphere



measuring oxygen in a high temperature gas. However, as it obvious from the equation (2), 1% change of oxygen is equivalent to 5% change of water vapor and therefore, a sufficient stability and S/N are required on the oxygen analyzer. As introduced above, Fuji Electric's zirconia oxygen analyzer has an outstanding stability, and therefore, is suited to be used as a hygrometer. With a dry air generator (used for reference) combined, a zirconia high temperature hygrometer can be formed.

In case of non-air atmosphere such a gas exhausted after burning, the component remained after eliminating water vapor differs from air components. In other words, percentage of oxygen differs from 20.93%. Even in this case, concentration of water vapor can be measured by inducing sample gas (from which water vapor is eliminated) into the reference side of the zirconia oxygen sensor instead of air, without being affected by the concentration of oxygen. *Fig. 10* shows a principle diagram for humidity measurement in non-air atmosphere. This measuring principle can be expressed by the following equation.

$$100\,P_1(O_2) = [100 - P(H_2O)] \cdot P_2(O_2) \quad \ldots\ldots\ldots (3)$$

where, $P_1(O_2)$: Oxygen in wet gas (Vol%)
$P_2(O_2)$: Oxygen in dry gas (Vol%)
$P(H_2O)$: Water vapor in wet gas (Vol%)

The following equation (4) can be established by applying equation (3) to equation (1), and from this equation, signals which depend only on water vapor (Vol%) can be obtained.

$$E = \frac{RT}{4F}\, ln\, \frac{P_1(O_2)}{P_1(O_2)/[100 - P(H_2O)]}$$

$$= \frac{RT}{4F}\, ln\, [100 - P(H_2O)] \quad \ldots\ldots\ldots\ldots\ldots (4)$$

The hygrometer of this method is suited to a measurement of humidity under a high temperature and high humidity condition for which the conventional hygrometer could not be used. In addition, this hygrometer features that the response is as high as the zirconia oxygen analyzer and that the standard gas containing oxygen can be used for calibration instead of standard humidity generator.

(2) General specifications

Measuring range: 0 to 30, 0 to 100 Vol% H_2O
Reproducibility: ±1% of the maximum output signal
Response: Air base . . . 90% response 10 sec or less
Non-air base . . . 90% response 30 sec or less
Output signal: DC 4 to 20 mA, isolated
Output signal characteristics: Linear for Vol% H_2O

(3) Applications of zirconia hygrometer

This hygrometer has been used for energy savings of heated dryers and high temperature moisture regulators and for product quality control at the following fields.

- Air dryer in paper mills (for energy saving)
- Food industry (bakery, instant noodle, buiscuit) (for quality improvement)
- Textile industry (Texture dryer, cloth dryer) (for energy saving and quality improvement)
- Tobaco industry (for energy saving and quality improvement)
- Building materials (plywood dryer) (for energy saving)

4 CONCLUSION

A solid electrolyte which uses zirconia for the base features its high ion conductivity and at present, there is nothing better than this. Sensors which use the solid electrolyte are available in addition to those introduced above. λ-sensors used to detect air-fuel ratio of automobiles have already been available in the market, and Fuji Electric is also practically manufacturing carbon sensors used to directly measure carbon potential of carbulizing furnaces. At present, the research and development of zirconia sensors are proceeded toward such a direction as to reduce dimensions, realize low temperature operation and to eliminate use of reference air. When these are completely developed, the fields of application will further be expanded.