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ENEA experience in oxygen measurements

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A B S T R A C T

Impurity detection in liquid metals is one of the most important tasks in the development of Accelerator Driven Subcritical (ADS) system technologies. Dissolved oxygen and metal oxides are the most dangerous impurities that could affect the Pb(44.5%)–Bi(55.5%) eutectic alloy cooling/target system, especially in consideration of the potential for system plugging. Accurate measurement of oxygen concentration in heavy metal coolants or targets for nuclear applications, whether liquid lead–bismuth eutectic or pure lead, is a critical issue in defining the need for active oxygen control to first of all prevent contamination of the liquid system by lead and bismuth oxides, and, in addition, to ensure efficient corrosion protection of iron-based alloy structures in contact with the coolant/target if the self-healing oxide layer method of corrosion protection is chosen. Due to this twofold aspect of the management of dissolved oxygen, the monitoring of oxygen concentration becomes of primary importance. This paper will focus on the development of an on-line oxygen monitoring system and more particularly on the description of the test to define the reliability of the electrochemical sensors. In addition, it will address the question of how such systems can be improved.

1. Introduction

The development of the heavy liquid metal chemistry control and monitoring is one of the issues that is critical for nuclear systems using lead alloys either as a spallation target or as a coolant [1–10]. Indeed, the relevant chemistry interacts with at least three operating specifications of any nuclear system; namely contamination control, corrosion control and radio-activation control, to ensure a safe management of the operations and maintenance phases.

Each of these three requirements has implications for chemical control in lead–alloy systems with respect to oxygen and other relevant impurities such as corrosion, spallation and activation products.

By using the ionic conduction properties of some solid electrolytes, and in particular zirconia-based ceramics, it is possible to make electrochemical cell assemblies that enable the measurement of dissolved oxygen in a liquid metal system. This is known as the electromotive force measurement in open circuits or as the galvanic cell method.

This technique presents several well known advantages such as:

- It is specific to dissolved oxygen, and bound oxygen, such as in oxide, is not taken into account.
- It enables a rapid and continuous sensor, that can be implemented directly in the system, provided leak tightness of the seal between the liquid metal and the ceramic can be obtained.
- It supports a wide concentration range in a single sensor as well as a potentially wide operating temperature range.
- There is no direct relation between the size and contact area of its associated electrodes.

In addition, the sensor allows measurements to be made with only minimal disturbance to the measured system and it can be used on a number of applications.

The main requirements for an effective on-line oxygen sensor are as follows: it must be accurate in the low oxygen concentration range that is expected to be encountered; and it must be reliable, predictable and safe for long-term nuclear operations. However, some limitations have appeared on some sensor technologies [10]; for example, ceramic sensors are relatively fragile, and many sensors reflect a time drift. Such limitations may delay for a while their direct implementation on nuclear systems.

2. Principle and theory

The oxygen sensors discussed in this paper are based on the electromotive force (EMF) measurement method at null current for a galvanic cell.

Such a cell is built with a solid electrolyte such as zirconia doped with either magnesia or Yttria. The dopant is needed to stabilize the ceramic into the tetragonal form, which allows oxygen

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ions to cross the electrode and to conduct electricity under conditions of fixed temperature and oxygen concentration.

In Fig. 1, the working principle of the galvanic cell is described: (1) is the reference electrode, with a constant Oxygen concentration (C_{O_2}), while (2) shows the working electrode which is immersed in the liquid metal phase where the unknown C_{O_2} is.

The method of electromotive force (EMF) measurement with null current can be applied to the measurement of the dissolved oxygen in liquid lead–bismuth alloys. A typical electrochemical galvanic cell that will be subsequently referred to as an EC sensor is as follows:

$$\text{Mo, Metal} + \text{metal oxide(reference)}ZrO_2 + Y_2O_3\ \text{Pb} + \text{PbO (lead alloys solution), steel} \qquad (1)$$

where the yttria stabilized zirconia (YSZ) ceramic, which conducts specifically oxygen ions, separates 2 medias showing different oxygen activities: an electromotive force is then formed across the solid electrolyte. If one of the media is defined to act as a reference, so as to maintain constant the oxygen partial pressure to a defined value, then the EMF is a function of the oxygen activity in the other medium.

Assuming pure ionic conduction in the solid electrolyte, and assuming that all transfers at the various interfaces developed in the electrochemical cell are reversible, the Nernst relation giving the theoretical EMF. can be written:

$$E_{th} = \frac{RT}{4F} \cdot \ln \frac{P_{O_{2(\text{reference})}}}{P_{O_2}} \qquad (2)$$

With E_{th} in Volts, and R is the perfect gas constant (8.31441 J/mol/K), F is the Faraday constant (96484.6 C/mol), T, the temperature (Kelvin) and P_{O_2} is the oxygen partial pressure in the media.

The choice of the reference system depends widely on various parameters, such as for instance the gas or liquid phase; liquid metals are known to provide a better contact with the solid electrolyte, providing a lower cell resistance at comparatively lower temperature. The use of low melting point metal favours the use of the sensor in a higher temperature range. In addition, the contact lead wire must be compatible with the liquid metal melt of the reference. The chemical compatibility with the solid electrolyte must be ensured as well.

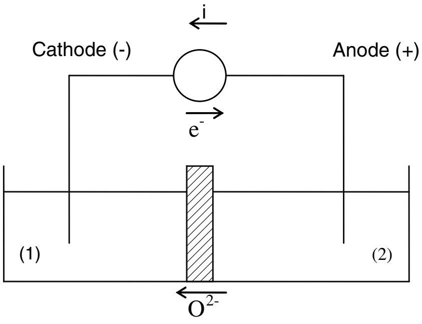

Fig. 1. Galvanic cell principle.

The ceramic electrolyte, which should be in contact with the melt alloy, is of a cylindrical shape. Its bottom is semi spherical.

The reference electrode and the metallic wire are hosted inside the electrolyte. The metallic wire is connected to the voltmeter.

It is possible to use different kind of reference electrode:

- Bi/Bi_2O_3 (mp. 271 °C), Mo lead wire;
- In/In_20_3 (mp.157 °C), Mo lead wire;
- Air, Pt lead wire.

Due to signal amplification problems detected for the Air/Pt sensor, the research programme was focused on the calibration of a Bi/Bi_2O_3 (Fig. 2) sensors supplied from IPPE, Obninsk (Russia) and the design and calibration of an In/In_2O_3 sensor(Fig. 2).

This analysis was performed for pure lead as well as for the lead–bismuth (55% in weight) eutectic (see Table 1).

2.1. Calibration experimental procedure

2.1.1. Oxygen Fine Measure experimental device

The OFM (Oxygen Fine Measure) calibration facility is a device built in order to test and improve electrochemical oxygen sensors for liquid metals in stagnant conditions. It consists of a cylindrical vessel, a heating system, an inert atmosphere gas bubbling system and an electronic multimeter.

The recorder registers the temperature of the vessel, the sensor signal and the gas pressure. The bubbling is performed with Ar coming from a pressured tank. The vessel has an interchangeable top with a swage lock sealing for the gas pipes and the sensor itself.

There are two kinds of vessel tops: a simple one for measures in reducing conditions and a more complex one for oxidizing-condition tests.

Table 1
Summary of experimental procedures

Step	Value
Temperature gradient	673 K–813 K
Temperature step	20 K
Gas inlet	Ar + H_2(3%)
Number of temperature tests	2
Total LBE volume	0.5 l
Vessel material	AISI 316L

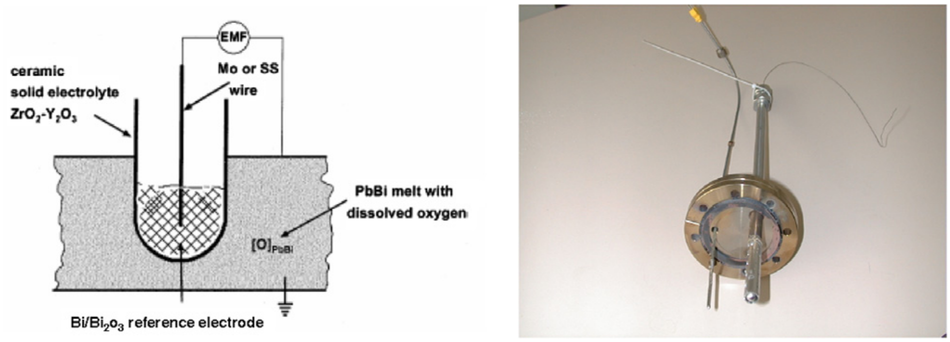

Fig. 2. Russian sensors ($Bi|Bi_2O_3$), produced at IPPE, Obnisk (sx) $In|In_2O_3$ sensor home produced (dx).

2.1.2. Test parameters

Two Bi/Bi_2O_3 reference oxygen sensors, as described above, made by IPPE [2], Obninsk, RU, were calibrated in the OFM facility, recording the EMF signal and their behaviour in different temperatures.

For simulating the CHEOPE III loop oxidizing conditions, i.e. an oxygen concentration of 10^{-5} to 10^{-6} wt%, solid Fe was added to the liquid Pb–55.5 Bi eutectic; to simulate the reducing LECOR environment, solid Mg was added and an oxygen concentration of 10^{-8} to 10^{-10} wt% was reached. The atmosphere was kept inert by means of Ar bubbling inside the vessel.

Two temperature loops were performed in order to check the reputability of the electrode signals.

The acquisition system for the CHEOPE III sensor was a digital one, while the one for the LECOR sensor signal was an analogical data recorder. This is why the EMF graphics are different and the calculation of a tendency line for the analogical graphics was necessary.

2.2. Calibration experimental results

After the calibration campaign, the data collected were plotted in order to compare the behaviour of the sensors in different environmental conditions.

They show a quite linear behaviour of the two sensors, in stagnant condition.

Fig. 3 summarizes the experimental results, comparing them with the calculated theoretical curves of FEM at fixed oxygen concentration. The iron oxide curve and the magnesium oxide one are emphasized.

It is possible to underline the good behaviour of both the sensors at different temperature plotting the output EFM signal parallel to the temperature variations.

Fig. 4 shows the sensor signal of the LECOR and the CHEOPE III loops.

2.3. Calibration conclusions

Both Bi|Bi_2O_3 sensors gave good agreement between expected and experimental data, in stagnant conditions. The EMF measured values were consistent with the predicted calculated ones giving an accurate behaviour, with an excellent agreement with the calibration standard for further work.

During the calibration campaign in Lead, it has been noted that the outcome signal does not vary too much then the one in LBE. Usually it is, at least, 10–20 nV less then the previous one for the same testing temperature.

3. Experimental data

After the calibration procedure the sensors were mounted in the LECOR and CHOPE loops.

3.1. LECOR loop data

3.1.1. Bi|Bi_2O_3

The historical reconstruction of the oxygen sensor signal during the four experimental runs ($T = 673$ K, constant) is shown in Fig. 5.

In the first run, before starting exposure tests, 130.8 g of Mg were added in 400 l ca. of LBE in order to guarantee reducing conditions. In the second run, after the conditioning in the storage tank with Ar + H_2(3%), the oxygen signal remained near 500 ± 100 mV. In the third run, the results show an oscillatory path near 500 ± 30 mV, even thought there had been a planned stop. In the fourth run the oxygen concentration grew consistently; to reduce this, a gas bubbling was performed, without success, and then Mg was added again.

It is notable the degree to which the oxygen concentration has an oscillating behaviour. This result has to be considered excellent, given that these variations are very small. In particular, after the LBE conditioning, the sensor signal starts from very high mV values and later lowers towards the acceptable value of 500 mV ca, indicating slightly greater reducing conditions than the minimal required signal (>350 mV).

3.1.2. Ini|In_2O_3

After the first 1400h, a historical reconstruction of the signal is possible. In Fig. 6 the reducing action observed in the first days in the storage tank is clearly visible. When the test campaign started, the injection of Ar/H_2 was stopped. In the graph it is possible to see how the oxygen content slightly increases.

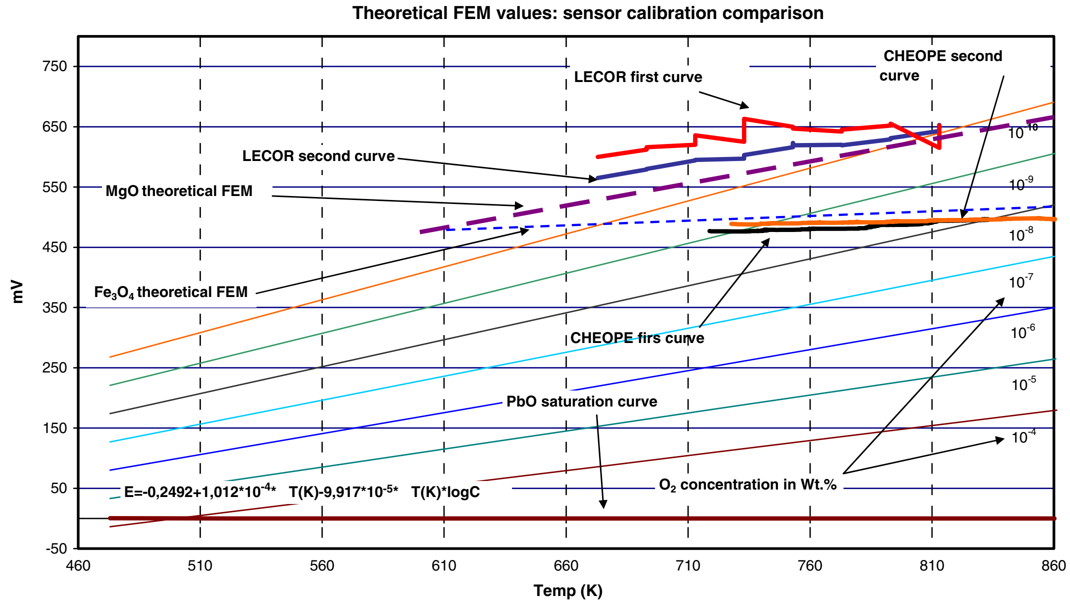

Fig. 3. Summary of experimental data and comparison with theoretical oxygen concentration/EMF curves.

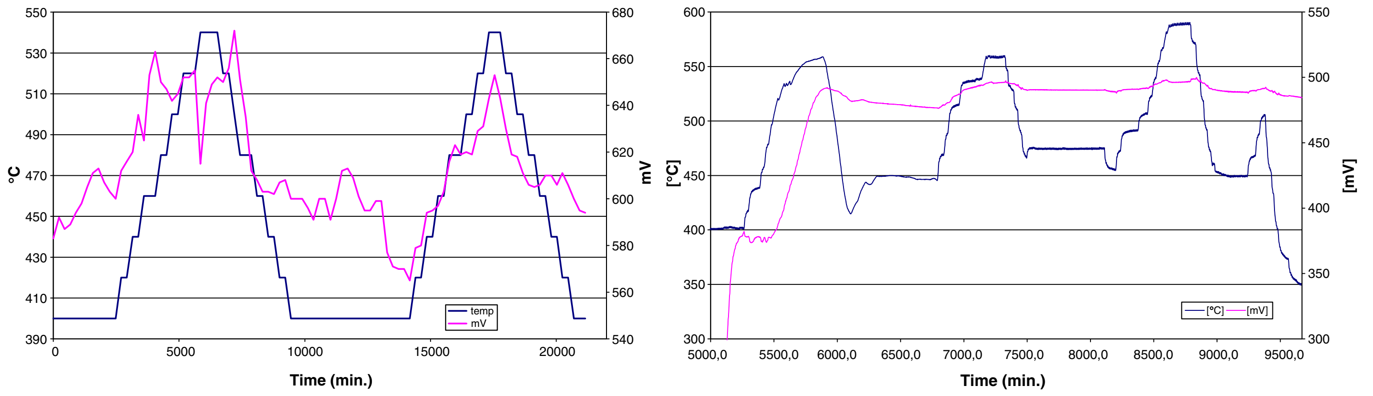

Fig. 4. FEM signal of the LECOR (sx) and CHEOPE III (dx) sensors and temperature variations.

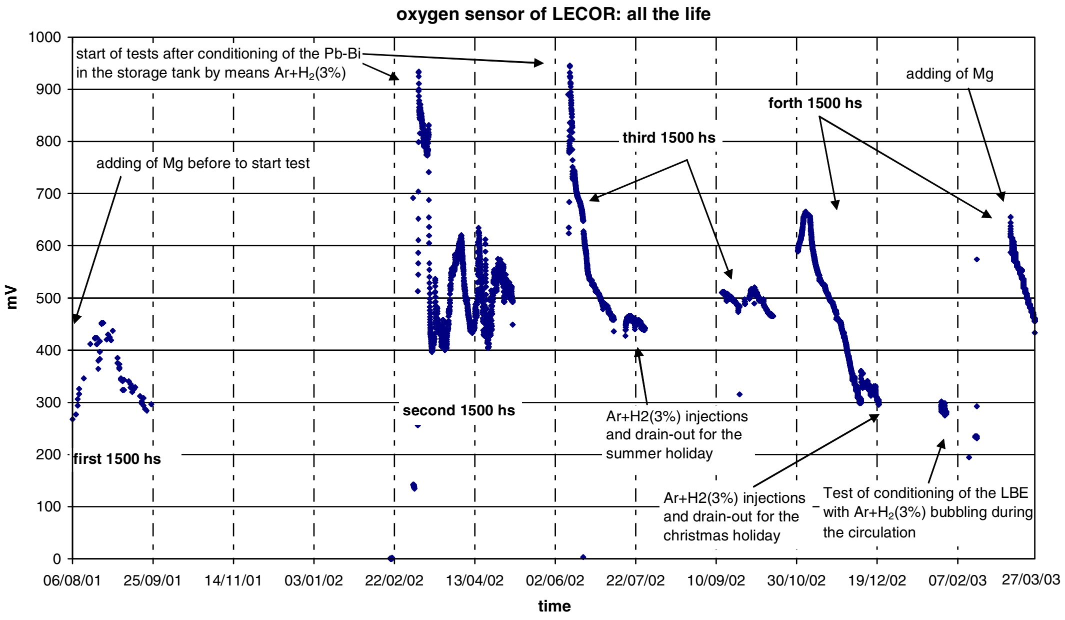

Fig. 5. Reconstruction of whole activity of LECOR sensor.

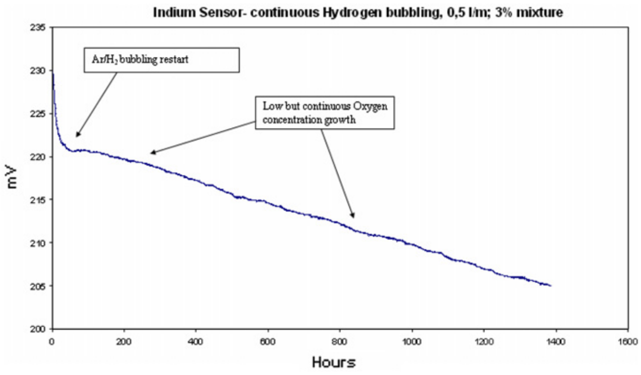

Fig. 6. Conditioning of LBE via bubbling of Ar–H_2 (3%) in the storage tank, with a flow of 0.5 l/h.

This is caused by the mass transfer between the passivated pipe walls and the reduced LBE.

A comparison between the behaviour of the two different sensors is shown in Fig. 7.

As can be observed, the output signal is in the first case positive and it grows up to a constant value (∼500 mV). Two slopes are clearly identified. They show two Ar+H_2 bubbling series. After the first one the O_2 content increased a little, while after the second one the oxygen content remains almost constant.

In the second case, the signal is negative and changes to positive values due to gas bubbling.

The two sensors, with very good agreement, show that the H_2 bubbling method is effective in order to reduce the oxygen content.

3.2. CHEOPE III loop data

In the CHEOPE III loop, 10,000 h of corrosion tests in lead bismuth were performed. During the whole duration of the campaign the O_2 content was measured with a Bi|Bi_2O_3 sensor and recorded.

After the conclusion of the tests the loop was emptied, cleaned and re filled with pure Lead in order to start another 10,000 h material compatibility test with a different liquid metal.

3.2.1. Bi|Bi_2O_3 in LBE

The historical reconstruction of the oxygen sensor (Bi|Bi_2O_3) signal of CHEOPE III loop (T = 673 K, constant) is shown in Fig. 8.

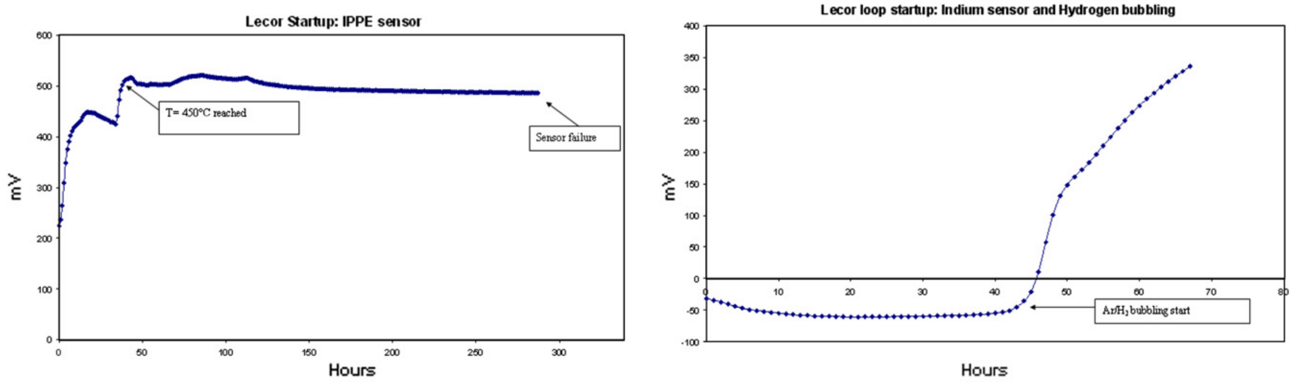

Fig. 7. Comparison between the start up of the Russian sensor and the ENEA's one.

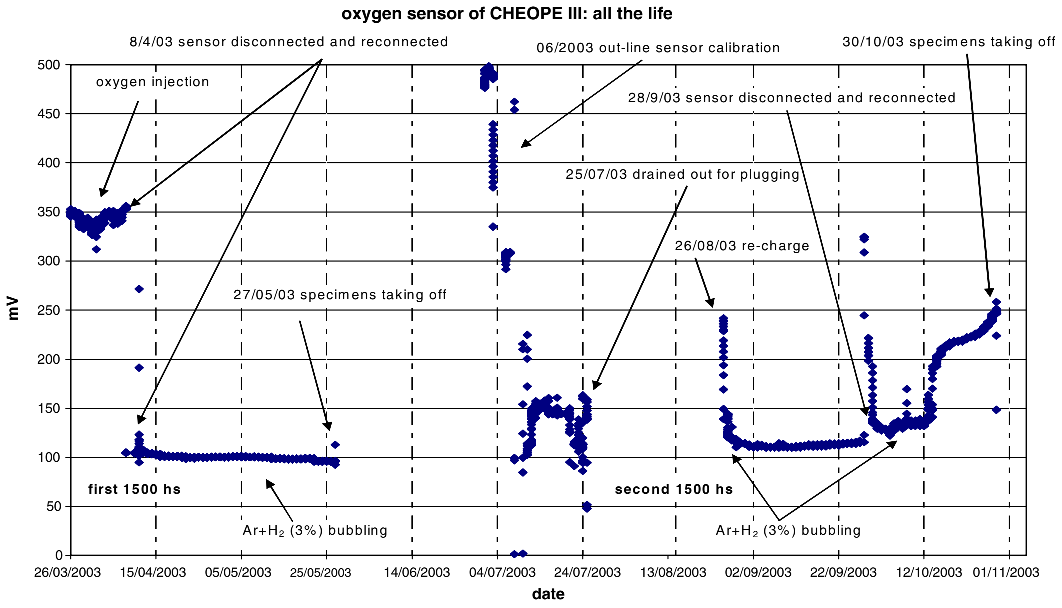

Fig. 8. Reconstruction of whole activity of CHEOPE III sensor.

The operating oxygen concentration range is 10^{-5} to 10^{-6} wt%, corresponding to a 150–200 mV signal ca. These conditions are very close to the saturation value for PbO (10^{-4} wt%, i.e. 76 mV ca.) and for this reason, exact control is very difficult. This could be seen comparing the two historical pictures of the two facilities: in the CHEOPE III one, planned stops and technical problems are much more frequent, where the following analyses of the impurities gave PbO as the main result. From this behaviour it is possible to infer that the sensor signal, even near the lead oxide saturation level, is reliable.

The sensor response to the on line gas bubbling is not immediate. Some weeks are necessary to stabilize the signal, as depicted in Fig. 9, showing the sensor signal after one month while some bubbling were performed.

3.2.2. Bi|$Bi_2O_{3.}$ in Lead

After the conclusion of the corrosion tests in LBE, in the frame of the 6the framework programme, the PbBi was substituted with pure Lead. This was done in order to perform new compatibility tests.

The Bi|Bi_2O_3 sensor installed in the plant was recalibrated and set in the third test section in order to monitor the content of the oxygen dissolved in the Lead, during the tests.

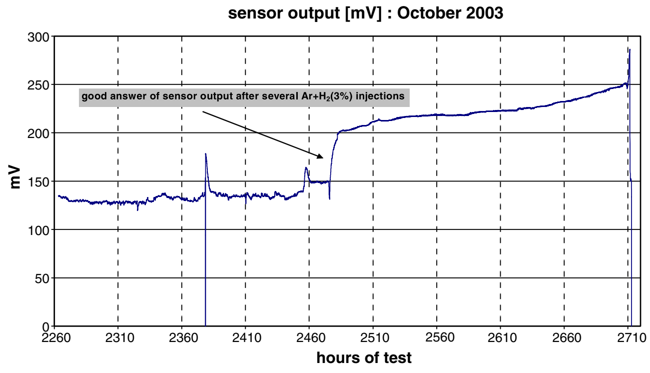

Fig. 9. Answer of the sensor output after several gas bubbling within one month.

In Fig. 10 the first 2000 h are graphed. It is possible to see that, during the first 500 h, the dissolved oxygen increased and then decreased after the injection on Ar/H_2. The gas mixture was bubbled for 10^5 min at a flow rate of 0.5 l/min. When the bubbling of the mixed gas was suspended the oxygen content increased.

It is possible to graph also the start up of the facility. During the first seconds the signal oscillates then after the pump started to

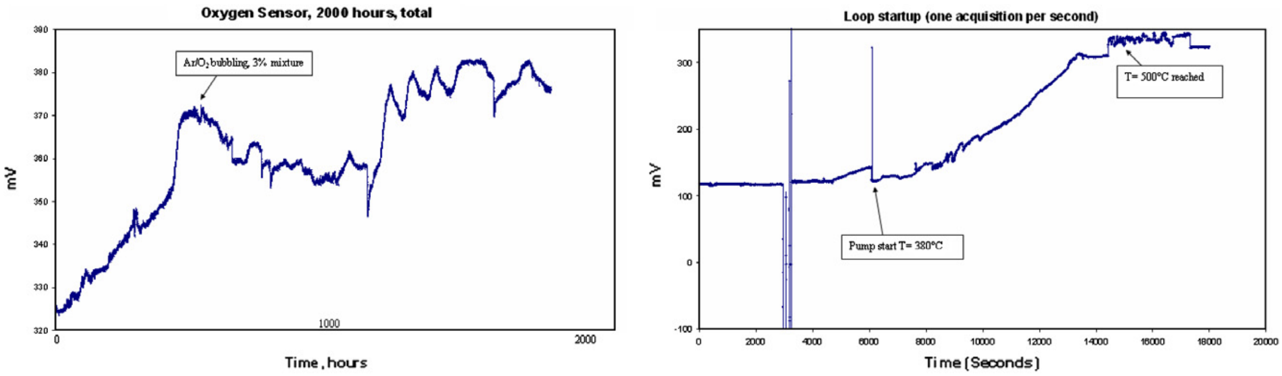

Fig. 10. Cheope III sensor historical outcome signal and start up.

work it grows up to 300mV. The signal becomes constant when the loop reaches the test temperature.

4. Conclusions

In PbBi, the two Bi|Bi_2O_3 sensors gave signals which were in good agreement with the theoretical ones in both plants. Also the In|In_2O_3 sensor gave outcome signals coherent with the theoretical data.

Moreover the two sensors gave coherent signals in similar working conditions, allowing the start of the design of a sensor for a pool configuration.

That led to the design and construction of an oxygen sensor adapted to pure Lead. In this case it was a technological innovation since, up to now, few data were available. The Bi|Bi_2O_3 sensor was recalibrated in pure lead and showed a behaviour comparable to the one in PbBi.

Only the magnitude of the outcome signal is slightly lower than in the case of LBE .

The next step is to design and construct an oxygen sensor for a pool type reactor. This sensor will be tested in the frame of experimental campaigns, which will be performed in the CIRCE facility next year.

For the new ‘pool’ sensor some obstacles must be overcome, such as the higher pressure field, the temperature variations and the insulation of the electrical cables.

As a matter of fact, in order to monitor the oxygen content in a pool nine metersdeep, it is necessary to install some sensors.

Due to the different depths, they are loaded differently along their length and this can affect the ceramic glove. Moreover the temperature gradient along the pool affect both the ceramic and the electrical cables with the possibility to break the sensor.

Acknowledgements

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