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Concettualizzazione del sistema di regolazione e controllo dell'ossigeno disciolto in sistemi nucleari a piscina refrigerati a Piombo

A. Gessi

Report RdS/2012/062

CONCETTUALIZZAZIONE DEL SISTEMA DI REGOLAZIONE E CONTROLLO DELL'OSSIGENO DISCIOLTO IN SISTEMI NUCLEARI A PISCINA REFRIGERATI A PIOMBO

A. Gessi - ENEA

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Titolo

Concettualizzazione del sistema di regolazione e controllo dell'ossigeno disciolto in sistemi nucleari a piscina refrigerati a Piombo

Descrittori

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Sommario

Il presente documento riassume l'esperienza acquisita dai laboratori di ENEA Brasimone sui sistemi di monitoraggio e controllo dell'Ossigeno disciolto nei sistemi a piscina refrigerati a metallo liquido. Tre sono gli argomenti di interesse, sviluppati in tre sezioni successive del documento:

1. I sensori Ossigeno
2. I sistemi di filtrazione delle impurezze solide
3. il sistema di controllo Solido/liquido

Note

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THE OXYGEN SENSORS

Based on the Russian work on important aspects of safe application of liquid lead (Pb) and lead-bismuth eutectic (LBE) as a coolant in nuclear reactors [1,2], it is generally accepted that maintaining a certain level of dissolved oxygen (oxygen potential) in these liquid metals significantly increases the compatibility with steels, the favoured materials of construction at temperatures below 650°C. Efficient control of the oxygen potential requires devices for adding oxygen as compensation for the consumption that results from steel oxidation [3] and oxygen sensors for monitoring the actual level of dissolved oxygen in crucial positions within the reactor. Furthermore, such sensors are mandatory for characterizing the conditions in material tests targeting the performance of steels in the respective liquid metal. The high chemical stability of ceramics makes electrochemical oxygen sensors with oxidic solid electrolyte especially appropriate for application in liquid Pb alloys. The need to measure the oxygen potential on-line motivated several studies on the performance of electrochemical oxygen sensors in liquid Pb alloys in the recent past [4–12].

The principal components of an electrochemical oxygen sensor are

(i) the solid electrolyte;

(ii) the reference electrode which exhibits a known and, at constant temperature, constant chemical potential of oxygen;

(iii) a second electrode (working electrode), the oxygen potential of which is to be measured.

The electrodes are in intimate electric contact with opposing sides of the electrolyte that transforms the difference in the chemical potential into a difference in electric potential. This difference in electric potential is transmitted to a high-impedance voltmeter via the electric leads of the electrodes.

In the case of measurements in liquid metals, the electric contact of the working electrode is easily accomplished by submerging the electrolyte in the liquid metal. The required separation from the reference electrode is achieved, e.g., by using an electrolyte tube that is closed at one end. An auxiliary electric conductor positioned in some distance from the liquid-metal/electrolyte interface bridges the gap between the liquid metal and the connection to the voltmeter. The reference electrode that resides inside the electrolyte tube is formed either by

(i) a partially molten mixture of a pure metal (liquid at operation temperature) and a thermodynamically stable oxide of this metal—and a submerged wire as electric lead, or

(ii) a gas with constant oxygen partial pressure combined with a wire contacting the internal electrolyte surface. Today, such oxygen sensors are routinely used for characterizing the conditions in experimental facilities operated with liquid Pb or LBE.

The sensor under development at ENEA for CIRCE is a device for control of oxygen content in Pb-Bi eutectic (as well as in molten Pb) and is designated for using in CIRCE circulating test facility.

The results of investigations conducted within the framework of several national and European programs (Ref. [1]) demonstrated that the most acceptable method of control of oxygen in liquid Pb and Pb-Bi is the method based on use of galvanic concentration cell (GCC) with solid electrolyte possessing ion-selective conductivity (relative to oxygen ions). With operating GCC, the thermodynamic activity of oxygen (a_0) in liquid metal converts to electric signal (GCC's e.d.f.). With known thermodynamic properties of GCC's reference electrode, the GCC's e.m.f. can be easily calculated at a high accuracy. If the reference electrode represents Bi and Bi_2O_3 mixture (the most probable reference electrode for sensor under development) the e.m.f. is determined by the relations

$$E\ (\text{в}) = 0{,}131 - 1{,}5\cdot10^{-5}\,T\,(1 + 6{,}61\,\ell g a_O) \qquad (1)$$

for liquid Pb

$$E\ (\text{в}) = 0{,}088 - 1{,}78\cdot10^{-5}\,T - 9{,}907\cdot10^{-5}\,T\,\ell g a_O \qquad (2)$$

for eutectic Pb-Bi.

Capsule-type sensor measuring thermodynamic activity of oxygen in liquid metal coolant, which is shown in Fig.1, is used as basis for the sensor under development.

In the upper part of sensor sealed lead-in 8 is positioned, where potential terminal 6 isolating the internal cavity of sensor from gas system of test facility is hermetically fixed. The sealed lead-in consists of an external sleeve and a co-axially placed internal electrode electrically insulated from the external sleeve by glass ceramics. The external sleeve of sealed lead-in is welded to sensor case 7. The sensor case is welded to metallic shell of ceramic sensitive element 1 connected to ceramic test tube 1 by means of high temperature glass ceramic 5. In the lower part of internal cavity of ceramic test tube, reference electrode (the mixture of bismuth 2 and bismuth oxide 3 (Bi-Bi_2O_3)) is located.

Basic Technical Performance of Sensor

Measurement range of a_0	from $1 \cdot 10^{-6}$ to 1
Pressure of medium under investigation, MPa, no more than	0,5
Flow velocity of Pb, Pb-Bi, m/s, no more than	1,0
The rate of temperature variation of Pb, Pb-Bi, °C/s, no more than	10
The range of temperature variation of fluid under investigation, °C	from 350 to 650
Limits of permissible relative deviation from nominal static characteristic (NSC), %	±10
Time required to achieve the operating conditions at first installing of sensor into fluid under investigation, hour, no more than	10
Overall dimensions of sensor, mm:	
length	3000 4000 8000
diameter	27

Oxygen activity sensor should meet the following design requirements:

- sensor should be resistant to mechanical action and vibrostrong;
- sensor design and used structural materials should be stable to temperature variations whose amplitudes and variation rates meet the conditions of sensor locations on CIRCE test facility;
- sensor design should provide its serviceability under the conditions of its constant being in liquid lead-bismuth within the given CIRCE test facility lifetime;

- electric connectors of the sensor should provide non-trouble operation under the conditions of temperature, pressure and ambient humidity meeting the requirements that are placed upon the environment of CIRCE operating areas;
- sensor design should rule out ingress of liquid lead-bismuth into a room at accident failure of its ceramic components.

The basic specific feature of CIRCE circuit design is that sensor must operate in liquid metal melt at large depths (up to 6 m).

At first, the base option of sensor (Fig.1) updated for possible submergence at a depth up to 5 m in molten lead (lead-bismuth) was tested. Measurements were taken at oxygen TDA (in molten lead) in the range from a=1, which corresponds sensor's e.m.f. E≈120 mV, to $a=10^{-4}\div10^{-5}$, which corresponds sensor's e.m.f. E≈420÷500 mV at temperatures of 480-540 °C.

Table given below lists parameters of liquid Pb as well as e.m.f. values and corresponding TDA of "reference" sensors installed in test section. Listed are as well the e.m.f. values and the corresponding TDA values of oxygen sensor with 5m.- long immersed part as a function of depth of immersion.

L, м	T, °C	V, m/s	$E_{ref.\ sensor}$, mV	$A_{ref.\ sensor}$	E_6	a_6
1	470	0,25	117	1	120	1
2	470	0,25	119	1	113	-
3	480	0,25	120	1	102	-
4	480	0,25	132	0,8	91	-
5	480	0,25	140	0,5	83	-
1	480	0,25	148	0,4	141	0,4

As evident from the data presented in the table, at a small depth of sensor submergence into melt (about 1 m), its readings are in fair agreement (with an accuracy of 5%) with the readings of reference sensors. However, as the depth of submergence into melt increases, its e.m.f. values are beginning to strongly departure toward decrease. In this case the absolute e.m.f. value becomes less than the possible theoretical values (120÷116 мВ) for Bi-Bi_2O_3 reference electrode which is used in oxygen TDA sensors.

The reason why readings are decreased is the reduction in the resistance of insulation of potential terminal being inside the sensor body, Fig. 1.

To eliminate the loss of sensor signal, the following changes are introduced into the base model design:

- a new design using sealed lead-in based on special temperature stable 2-shell metallic cable is developed;
- a special system is developed to measure sensor signal and form a guard potential equal to the level of valid sensor signal on the intermediate shell of potential terminal cable, to protect the valid sensor signal against loss.

In the process of further justification of sensor design the geometric dimensions of separate components and sensors on the whole were refined, and requirements to materials used in sensor were formulated.

Sensor can have several modifications differing in length of the immersed part and the presence (or absence) of reducer for welding. The general view of refined oxygen sensor design for which working drawings have been developed is shown in Fig.2.

The sensor under development consists of ceramic sensitive element (CSE) 5 (material - ZrO_2 Y_2O_3) as capsule with 12 mm outer diameter, 4-6 mm inner diameter and 15-20 mm length. Capsule is connected with metallic CSE casing 3 by means of high temperature sealant which is to provide air-tight strong and reliable connection. Metallic CSE casing 3 is welded to sensor body 4. There is a Bi-Bi_2O_3 reference electrode (where the predetermined partial pressure of oxygen is maintained) inside CSE. In the upper part of sensor sealed lead-in 2 is located, which is welded to casing 4 and designed to make the internal pool of sensor leak-proof. Besides, the sealed leak-in is designed to prevent issue of alloy outside into operating areas in the case of the capsule failure. Two-shell potential terminal lead 1 implements electric contact between reference electrode 2 and measuring block 6 and protects valid signal of sensor from loss.

Hermetic sealing of sensor installed in circulating test rig is planned to be effected using potential terminal cable by means of fluoroplastic seals in the “cold” zone.

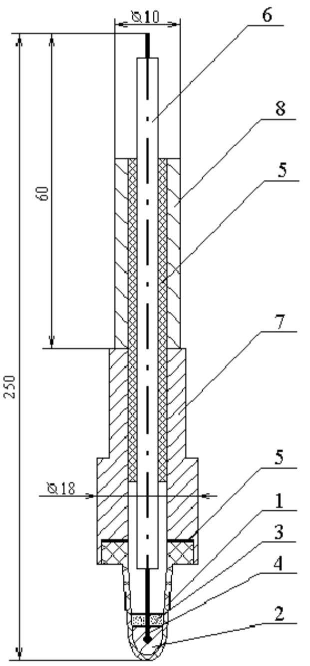
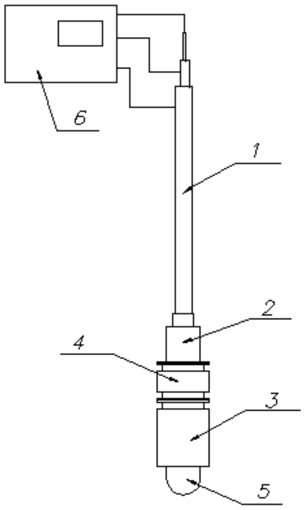


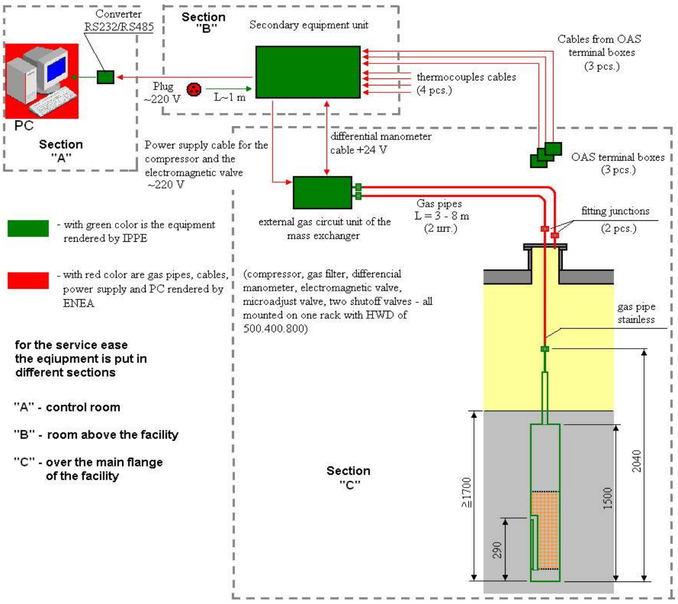
Fig. 1 – Base design of oxygen TDA sensor. 1 – CSE; 2- bismuth; 3 – bismuth oxide; 4 – electrode; 5 – glass ceramics; 6 – potential terminal; 7- casing; 8 – sealed lead-in.



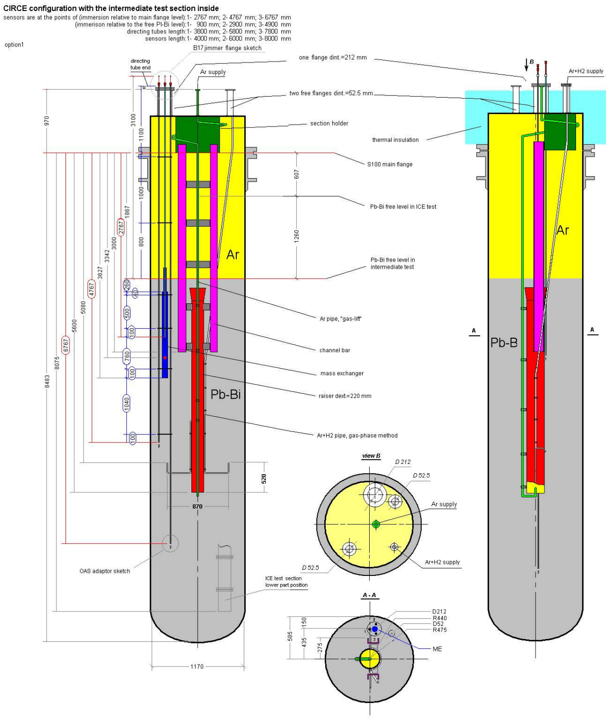
1 – two-shell potential terminal lead; 2 – sealed lead-in; 3 – metallic casing of ceramic sensitive element; 4 –adapter (transition part); 5 – ceramic sensitive element; 6 – measuring system with former of guarding potential.

Fig. 2. Oxygen TDA sensor

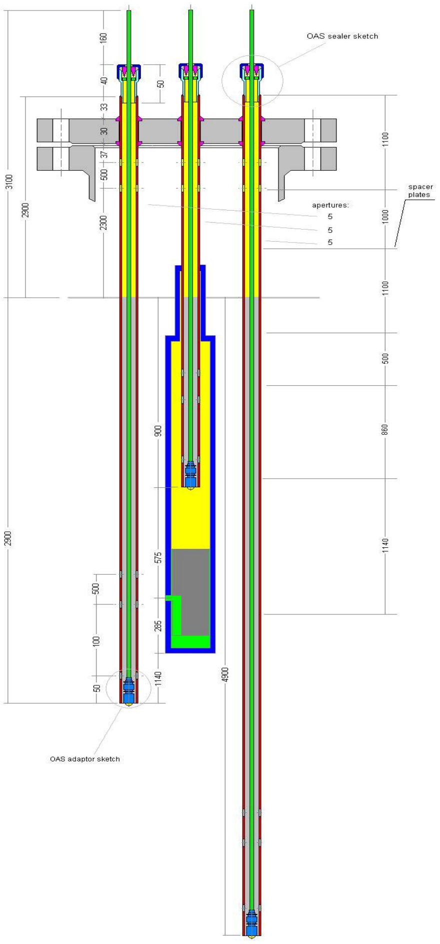
The sensors have been installed and set in the new section of the CIRCE pool facility. A new software was installed and implemented, as shown in the following pictures.

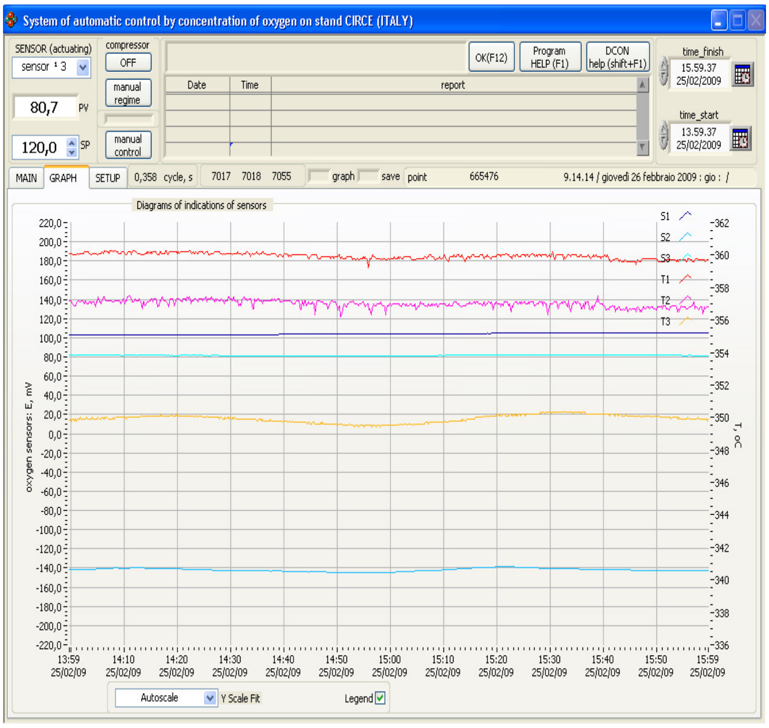


System scheme



The CIRCE setup





System of automatic control by concentration of oxygen on stand CIRCE (ITALY)

SENSOR (actuating): sensor ¹ 3

compressor: OFF

80,7 PV

120,0 SP

time_finish: 15.59.37 25/02/2009

time_start: 13.59.37 25/02/2009

0,358 cycle, s

7017 7018 7055

point 665476

9.14.14 / giovedì 26 febbraio 2009 : gio : /

Autoscale

Legend ☑

the test section.

Screenshot of the three CIRCE sensors

The experimental campaign consisted essentially into two separated goals: the validation of the full system and the model of Oxygen concentration in a large HLM pool. The screenshot of the acquisition system software is the confirmation of the accomplishment of both the two goals.

The electrochemical sensor gave expected outputs: the CIRCE melt had never been treated, conditioned or modified, so it was expected to find a signal proportional to an almost Oxygen saturated environment, i.e around a value of 180mV.

FILTERS FOR SOLID IMPURITIES, EXPERIENCES IN LOOP FACILITIES

The liquid Pb, can be considered a high dispersion suspension of extremely fine particles of Pb, Bi, Fe, Cr, Mn oxides. As a function of experimental conditions, their concentration could be dangerous for the coolant use, possibly causing the separation of powders and slags of oxides near valves, pipes elbows, heat exchangers walls, with the possible risk of the plugging of the whole liquid metal loop system. These oxides form mainly due to excess of oxygen in the melt, coming from small leakages, failures in the oxygen control or problems from the original solid LBE or Pb ingots.

These phenomena have been seldomly observed in the ENEA loops (LECOR and CHEOPE) in which the liquid melt LBE and pure Pb are used for corrosion studies. Lead oxides as very thin black dust was observed in outgassing systems, while solid slags, mainly consisting of lead oxide and intermetallic compounds, created some problems in the CHEOPE loop, when the loop was run with LBE, where the oxygen concentration was kept between the interval 10^{-6}-10^{-5} wt%, corrisponding to the Iron oxidation Gibbs free energy and just below to the Pb one (about 10^{-4} wt%), at 400°C and a flow rate of 1 m/s ca.

The CHEOPE loop has been used for more than 10000 hours of experimental campaign for materials compatibility studies, as far as corrosion problems of structural steels with oxygen passivates surfaces are concerned. These experiments have been performed in LBE and pure Pb. The steels passivation is the reason for the relatively high oxygen content, which was controlled by means of gas bubbling and monitored by electrochemical sensors. Difficulties related to the oxygen control and small oxygen leakages during the corrosion specimen extraction, could be considered the most probable causes of some slags formation during the LBE experiments. These solid slags did accumulate on the hot part of the loop (which is non-isothermal) where they sticked near a pipe elbow. The compostion of one of these slags is summarized in Table 1.

The presence of such macroscopic slags inside a liquid metal loop can cause flow rate reduction, problems in controlling the dissolved oxygen and thus the experimental conditions for the corrosion tests, as well as possible plant plugging

problems.

Their composition and the nature of the phenomenon causes suggest also that the formation of oxides is a continuous one. The role of intermetallic compounds like Pb_7Bi_3 has also been found to play an important role. The use of on-line continuous filtering techniques gathers a very high importance.

On the other hand, during the pure Pb experimental campaign, very small problems of coolant pollution were observed. After 5000 hours of in situ passivation experiments performed at 500°C, with the same conditions of the previous campaigns, no macroscopic slag was observed, and the production of the so called "black dust" was heavily reduced. Filters and purification devices were implemented also.

The variability of the slags and powders dimentions, suggests that the best filtering approach is the use of "capillary" layers, oriented mainly perpendicularly to the liquid flux, thus creating micro stagnant areas where the coagulation of slags and their separation is enhanced. According to Y. Orlov et. al. the best suggested material for filtering material is a multilayer glass fiber tissue, with 95 wt% ca. of SiO_2 . Its high temperature stability (> 500°C) and the calculated filtering efficiency (0.9-1.1g-PbO/cm^3) are the reason for this choice.

A mechanical kind of filter was also tested. It consists of a three steps filtering device in which three poral filters of different meshes are set. The meshes are respectively: 50µm, 30µm, 20µm, where the largest one is the first encountered by the LBE flow. A similar mechanical filtering system, having meshes of 30µm, 20µm and 10µm was used during the filling of the CHEOPE III loop, keeping the temperature at 400°C .

The filters were built in the ENEA Brasimone laboratory, using AISI 316L steel and a commercial fiberglass. The fiberglass one was also equipped with a termocouple.

It was put in a pipe in the hot part of the CHEOPE loop and kept at 400°C. Then the loop was started for the experiments in flowing HLM, with the LBE kept at 400°C, the pure Pb kept at 500°C and the flow rate at 1m/s. The oxygen concentration was actively controlled by means of gas bubbling and monitored by electrochemical oxygen sensors developed and built by IPPE, Obnisk and by ENEA Brasimone. Oxygen concentration was kept at 10^{-5} wt% ca. The composition of the filtered partcles, as the one of the macrospic slags, was determined by means of a Thermo-ARL Xray fluorescence spectrometer and of a Philips X'Pert Xray diffractometer for powder samples.

The mechanical filter was simply put between the melting tank and the CHEOPE III loop, thus filtering 300 litres ca. of HLM at 400°C. During this operation a blockage of the 10 µm mesh by oxides was observed only during the LBE experiments. The device was then dismounted and photographed A bypass pipe line was built in parallel to the filtering device.

The filtering disks were then replaced by a sintered tube of PORAL type having larger filtering surface (D=40mm, L=250mm, mesh=20□m). The results were acceptable, therefore it was used also for the initial LBE filling of LECOR (500 l) and CIRCE (7000 l)

During the 10000 hours corrosion experiment performed in the CHEOPE III loop, no flow rate decreases were observed. The oxygen probe signal remained quite stable, corresponding to the oxygen concentration required of 10^{-5} wt% ca (fig. 9). No plugging problems happened. No additional reducing gas bubbling was required.

After the draining of the loop, in both experiments the fiberglass filter was dismounted. It appeared clean and no macroscopic slags were observed The fiberglass containers were disassembled too and the solid particles trapped in it were separated and analyzed by means of X ray diffractometry and fluorescence technique. The composition in LBE is similar to the composition of the slags that were found in the loop without the filter. Again, no slags have been observed in flowing Lead, where the amount of filtered particles appeared to be extremely low.

The three porals array cleaned without plugging problems all the LBE melted during the filling of CHEOPE III. All macroscopic slags were stopped by the mechanical barrier. The pipe was not plugged and no bypass line was used.

The implementation of such devices in a pool type system appears on the other hand not straightforward: the system must be coupled with sensing systems and PbO pellets Oxygen donors.

THE PbO PELLETS SYSTEM

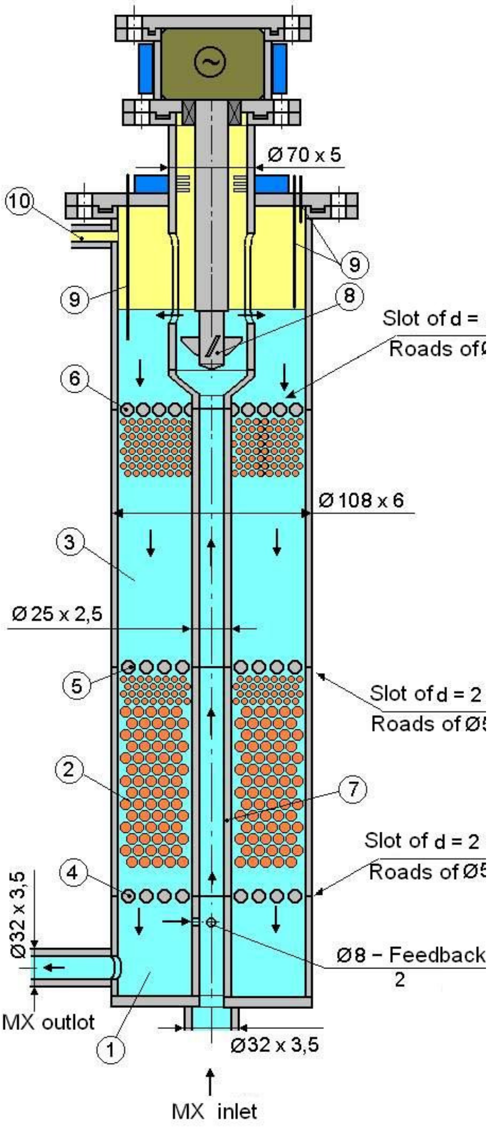
A promising method for actively controlling dissolved Oxygen in a pool system, given the relative unsuccessful Gas/Liquid approach, is represented by the PbO mass exchanger. The main parameters of a device based on the chemical equilibrium $PbO = Pb + ½ O_2$ are summarized as follows:

- Need of fluid saturated deviation to prevent Fe-Cr oxides reaction with the pellets
- O_2 supply driven by flow rate and temperature
- Large device ≈ 15-50 kg PbO(1 - 3.5 kg O)

- EFIT 9 g O /h (example)
- One filling per 4 – 16 days
- Several devices are needed per auxiliary loops or cartrides

Several filling operations per year even for *oxidation rate one order of magnitude lower*

- Use of the mass exchanger on an auxiliary loop (possibility to)
- Maintenance : problem of activated products in cold areas (^{54}Mn, ^{60}Co)



Scketch of a suggested PbO mass exchanger for a pool type.

The solid/liquid approach in Oxygen control appears to be more effective than the gas/liquid one, mainly due to the favourable kinetic of the reaction and due to the larger contac area between the solid donor/getter and the HLM.

CONCLUSIONS AND OPEN POINTS

Oxygen supply appears to be difficult at large rates in classical devices, due to th eneed to condition large bulks of HLM, [O] stratified :

- Gas phase supply would need further experiments to demonstrate the ability of large exchange coefficient
- Solid phase supply was not clearly demonstrated

Purification techniques have been defined and tested in loops, but filtering devices for Pools are still to be effectively located and implemented. All the safety issues connected with the introduction in the system of potentially radiological dangerous species need to be further investigated.

Moreover, on Oxygen sensing, because of non homogeneous concentration, it is necessary to use at least three sensors. They shall be placed in the coolant flow in the zones with maximum, minimum and intermediate temperatures (supposedly, in the range from 460 to 540 °C).

If there are zones with low rate of coolant temperature variation at their outlet, it is reasonable to install additional sensors.

As a summary, the control/monitoring of Oxygen in aHLM pool still represents a big challenge. The basic techniques have been separately investigated, their implementation in an integrated pool system is still to come.

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