Gas purifiers for closed-loop gas systems

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Abstract

Results on a study on the filtering system used at the CERN Closed Loop recirculation gas plant currently in test at CMS experiment at the LHC are reported. This study is focused on the regeneration processes of the metals - including both oxidation and reduction reactions of Copper, Zinc and Nichel – and on the thermodynamics of the regeneration reactions. This study confirms the filtering system efficiency towards the O_2. The findings of this study allow us to propose an optimized use of the purification system.

XI workshop on Resistive Plate Chambers and Related Detectors (RPC2012)
INFN-Laboratori Nazionali di Frascati, Italy
February 5-10, 2012

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[1] Speaker

1. Introduction

Resistive Plate Counters (RPC) are used in the muon detector of the Compact Muon Solenoid (CMS) experiment [1] at the CERN Large Hadron Collider. RPC use fluorine-based gas mixture whose main component is Freon. Because of the high cost of Freon and the very large gas volumes involved in the full system, the design of the CMS RPC gas system is based on a recirculation system called the Closed Loop (CL) .

The absence of gas contaminants is of paramount importance in all gas detectors, and especially in RPC due to the high reactivity of F-based gas mix used [2, 3]. A gas gain monitoring system [4] has been designed, built and being commissioned by the CMS RPC group for the fast and accurate monitoring of the working point, based on monitoring of the avalanche charge and of the chamber efficiency. The gas gain monitoring system is based on three single-gap RPC subdetectors flushed with clean gas mixture, CL mixture after purifiers before crossing CMS RPC, and CL mixture from the return lines. The gas gain monitoring will provide a warning in case of a working point change [5].

A gas quality monitoring system is being developed by the CMS RPC group and it will perform chemical analyses such as Gas Chromatography (GC), High Pressure Liquid Chromatography (HPLC), pH meters, etc. following the warning condition released.

No aspect of the chemistry of purifiers used in CL is fully understood, nor the extent or the nature of contaminants with the exception of fluoridric acid, whose presence is established. Tests [6, 7] at the Gamma Irradiation Facility (GIF) [8, 9] showed the presence of HF, which is detected by accumulation methods or by the use of HPLC, or ionic column-equipped GC. A systematic investigation has been proposed aimed to fully clarify the chemistry of purifiers used in the CL[10]. Purifiers and filters were studied at the ISR test area during chamber testing with cosmic rays [6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17] This study is focused on characterization of metallic filters reactions during filtration and regeneration in the CL.

2. Filters

With the original selection criteria being the filtering of H_2O and O_2, tests at GIF showed GC peaks of unknown pollutants that disappeared after the following purifiers:

- purifier 1: consisting of a 24-litre cartridge filled with 5A-Type molecular sieve manufactured by ZEOCHEM
- purifier 2: consisting of two 24-litre cartridges, each filled with a combination of metal filters:
  - Cu-Zn filter type R12 manufactured by BASF
  - Cu filter type R3-11G manufactured by BASF
- Purifier 3: consisting of Ni AlO3 filter type 6525 manufactured by LEUNA. This purifier has been removed at the time of preparation of this paper.

2.1 Metals

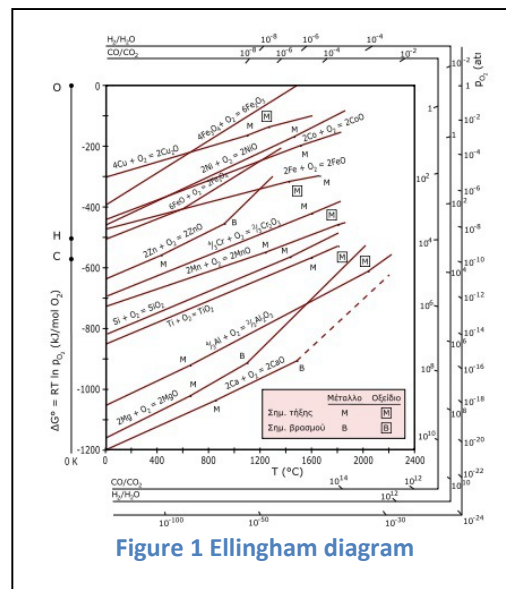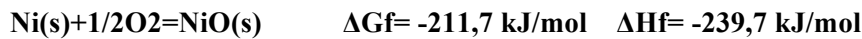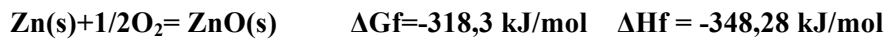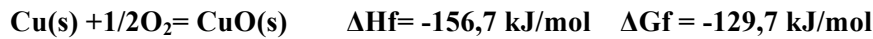Metals oxidize according to the following reactions:

2Cu(s)+1/2O$_2$= Cu$_2$O　　**ΔGf -147.8 kJ/mol,**　**ΔHf =-170.6 kJ/mol**

Cu(s) +1/2O$_2$= CuO(s)　　**ΔHf= -156,7 kJ/mol**　**ΔGf = -129,7 kJ/mol**

Zn(s)+1/2O$_2$= ZnO(s)　　 **ΔGf=-318,3 kJ/mol**　**ΔHf = -348,28 kJ/mol**

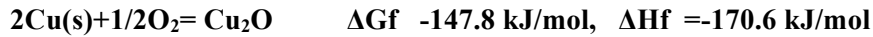**Ni(s)+1/2O2=NiO(s)**　　**ΔGf= -211,7 kJ/mol**　**ΔHf= -239,7 kJ/mol**

Figure 1 Ellingham diagram

The Ellingham diagram (Fig.1) shows the high tendency of metals to oxidation. Thermodinamic parameters are calculated at 25°C.
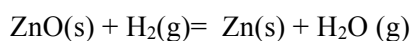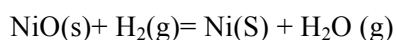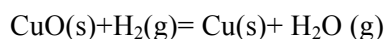
2.2 Regeneration

Metal filters are located as pellets inside the cartridges. Filters are provided as oxides, thus needing a regeneration before first use. The regeneration procedure consists of the following steps:

- A Noxal[2] mixture flows through the cartridges, while it is gradually heated up to 150°C;
- Further increase in temperature up to 215°C
- Noxal flux stops; a fresh inert gas fluxes through the pellets until they reach room temperature.

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[2] Gas mixture made of Argon and H$_2$ (20%)

Since the materials' reduction has never been extensively studied in this system, a preliminary thermodynamic approach of the involved reactions was performed

$Cu_2O + H_2(g) = CuO(s) + H_2O\ (g)$

$CuO(s) + H_2(g) = Cu(s) + H_2O\ (g)$

$NiO(s) + H_2(g) = Ni(S) + H_2O\ (g)$

$ZnO(s) + H_2(g) = Zn(s) + H_2O\ (g)$
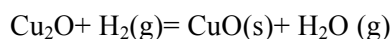
2.3 Thermodynamic study

A first approach to the theoretical utility of the regeneration process used has been proposed starting from a thermodynamic study.

With the help of HSC Chemistry simulation software, in Fig. 2 is reported a graph of free energy versus temperature referred to the reactions between oxides and hydrogen, based on their data of enthalpy, entropy energy and equilibrium constant values of CuO, Cu_2O, ZnO and NiO. The temperature range in the simulation includes those used in the regeneration; the thermodynamic variables are calculated in steps of 20°C.
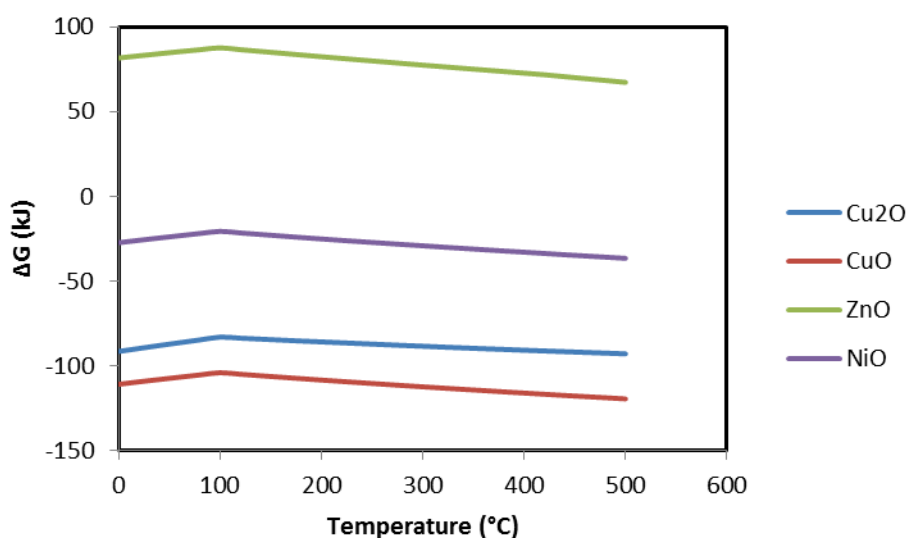

Figure 2 Free energies trend for all four reduction reactions.

The most spontaneous reaction in the range considered is that of CuO. As Figure 2 shows, the free energy trend is up to 100 °C increasing and then begin to decrease with the increasing in temperature. The different behavior is due to the presence of H_2O vapor after 100 °C that implies a higher value of entropy.

3. Conclusions

The literature research performed [18-30], allowed us to formulate the following considerations

1. Filter CuO R3 11G

Thermodynamic simulations highlight that R3 11G filter mainly oxidizes to Cu_2O. From literature data we state the time needed to reach a 0.9 conversion of CuO:

- at 148°C the kinetic constant k_0= 0.026 min^{-1} and the time needed is 95.6 min;
- at 216°C the kinetic constant k_0= 0.154 min^{-1} and the time needed is 16.1 min.

so the regeneration process can be optimized. Since the reduction time depends on the oxide mechanism formation, we can carry out the first regeneration in the worst condition. According to the data found in literature, k_0=0.0415 min^{-1} at 190°C is the smallest value of the kinetic constant. A 59.9 min time is necessary to reach a conversion of 0.9 in these conditions.

For later regenerations, we can assume that CuO is formed through a Cu_2O oxidation; in such a case the regeneration can be carried out at 215°C for 20 min to have a conversion >0.9.

2. Filter ZnO R3 12

It has the main aim to stop sulfur and arsenic eventually contained in the gas flow. These elements react with the filler in an irreversible way. When the amount of sulfur and arsenic in the gases will be known, we will be able to value the filler's life time.

3. Filter Ni-Al_2O_3 Leuna 6525

Even the NiO regeneration process could be optimized. In fact at 215°C, with the kinetic constant k_0= 0.15 min^{-1}, after 15.4 min we reach a conversion of 0.9.

This purification step was redundant since it worked in the same way of the first step. It has already been removed from the CL of the RPC detector of the CMS experiment.

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