ABSTRACT
Thermogravimetric systems running in the low-enthalpy range have been analysed. The carrier fluid is demineralized water coupled with a perfluorocarbon PFC or a hydrofluorocarbon HFC that operates as the working fluid. Minimum cycle temperature has been fixed, equal to $T_{\text{min}} = 30 \, ^\circ\text{C}$, while the maximum cycle temperature $T_{\text{max}}$ varies in range $60 - 90 \, ^\circ\text{C}$. As usual, pressure drops in the upward two-phase flow column have been evaluated as the sum of three terms: gravitational, accelerative and frictional. For several operating couples water-working fluid plant height $Z$ and plant power $W$ as well as the corresponding hydraulic efficiency $\eta_{\text{hy}}$ have been quantified. Among the different solutions analysed in the present paper, the couple water-PP 50 seems to result the most significant.

1. INTRODUCTION
Several years ago, at Politecnico of Milano, a wide research dealing with the performances and the characteristics of a non conventional thermodynamic converter was carried out. Such system, called thermogravimetric is capable of producing mechanical-electric energy through a thermodynamic process. The schematic diagram of a thermogravimetric system and its possible theoretical cycles are reported in Fig. 1 and 2, respectively: they have been widely described in previous papers [1, 2, 3]. During the first years of this research, the thermogravimetric plant was basically investigated for applications in the low enthalpy range: in this field, the system preferably runs with the so called saturated cycle and natural hot waters (80-120°C) could be exploited as the thermal source. Demineralized water was chosen as carrier fluid and the vapour of a chlorofluorocarbon (CFC) or of a hydrochlorofluorocarbon (HCFC) was considered as working fluid. In the following years sophisticated calculus codes able to analyse the conditions and the behaviour of thermogravimetric systems both in nominal and in off design conditions were realised. Thanks to these investigations in 1979 a thermogravimetric test plant was built next to the geothermal power station at Castelnovo Val di Cecina in the ENEL Larderello District. This test plant worked with demineralized water (carrier fluid) and R-114 (working fluid) with a two-phase duct of 446 mm: the experimental field lasted more than one year and proved to be very satisfactory [4, 5]. In the following years, a new analysis dealing with thermogravimetric plants operating in the medium-high enthalpy range (150-450°C) was carried out and other types of thermogravimetric systems were pointed out. Employing such temperatures a reduction in the plant height will be required: that can be obtained either by utilising a carrier fluid with an elevated density (lead or low-melting-alloys) or modifying the thermodynamic cycle by introducing the superheating. The possibility of operating with another series of working fluids was taken into account: in the meanwhile, due to their high ODP, CFC and HCFC had been replaced with PFC (perfluorocarbons) and HFC (hydrofluorocarbons), respectively. The solution of employing carrier fluids with higher density had been also considered, as cited above. In such context, that is the medium-high enthalpy range, two types of thermogravimetric plants resulted to be particularly promising: the first operates with the couple Pb-H$_2$O and the second with the couple Pb-PP50 [6, 7]. It is worth mentioning that the thermal source could be provided by the exhaust gases from large reciprocating engines or from gas turbine cycles. Scope of the present work is to newly investigate the low enthalpy range, still utilising demineralized water as carrier fluid but coupled this time with a PFC or a HFC.
2. FURTHER INVESTIGATIONS AND CALCULUS SCHEME

As widely explained in previous works the performances of a thermogravimetric plant basically depend on the properties of the working fluid, once fixed the extreme temperatures and the carrier fluid, here demineralized water. The use of water is primarily due to the operation temperatures as well as to other characteristics: low cost, non inflammability, non toxicity and total absence of environmental effects. As the minimum cycle pressure \( p_{\text{min}} \) must be higher than the vapour pressure of the carrier fluid (water) at the operation temperature \( (T_{\text{max}}) \), the choice in working fluid is remarkably restricted. Furthermore, chemical compatibility, thermal stability, low values of ODP and GWP must be also taken into account. All that considered, PF 5040, PF 5050, HFC 134a and HFC 125 have resulted to be the most promising ones.

Taking into account the numerous physical phenomena, the following chief working hypotheses were introduced into the present calculus scheme:

- Adiabatic contour
- Isothermal expansion of the working fluid in the two-phase flow duct (due to a large difference in the thermal capacity between the two fluids)
- Isobaric process of heating-evaporation and cooling-condensation of the working fluid
- Frictional effects for the carrier fluid along the downward duct LD (Fig. 1)
- Total pressure drops \( (\Delta P) \) of the two-phase flow along the T-PD duct (Fig. 1) evaluated as the sum of three terms: frictional \( (\Delta P_f) \), accelerative \( (\Delta P_a) \) and gravitational \( (\Delta P_g) \), i.e.

\[
\left( \frac{dP}{dl} \right)_f = \left( \frac{dP}{dl} \right)_a + \left( \frac{dP}{dl} \right)_g
\]

and consequently \( (\Delta P) = \int_0^Z \left( \frac{dP}{dl} \right)_f \, dl \).

The first ones have been evaluated by Davis correlation because it evidences, through Froude number, the diameter effect that is rather remarkable, due to the large size ducts. Due to the rather small pressure variation \( \Delta p = p_{\text{max}} - p_{\text{min}} \) along the two-phase column T-PD (with the consequence of a limited isotherm expansion of the working fluid) and due to the relatively low maximum cycle temperatures \( T_{\text{max}} \), the accelerative pressure drops \( \Delta P_a \) will be of a small entity. It is worth noticing that, on the contrary, such effect heavily affects a thermogravimetric system running with a high
density carrier fluid operating at an elevated temperature, with the consequence to drastically limit the system performances [7]. The void fraction is evaluated by El-Boher correlation [8]: this one has been also verified through experimental data obtained in the above cited thermogravimetric pilot plant of Larderello [9]. A peculiar aspect of the thermogravimetric system is the partial evaporation of the carrier fluid along the two-phase duct: such entity is rather high when the carrier fluid vapour tension is not far from the minimum cycle pressure $p_{\text{min}}$. However, the heat absorbed along the T-PD duct during such process is partially recovered in the regenerator: therefore, as a first approach, partial evaporation effect has not been considered in the present paper. The following calculus procedure was developed: $\Delta p = p_{\text{max}} - p_{\text{min}}$ (Fig. 2) is imposed and shared along the T-PD duct in one hundred partial $(\Delta p)_i$. $D_{\text{T-PD}}$, $R$, $V_{\text{LS}}$ have been considered as further independent quantities: $R$ is the mass flow rates ratio between the working and carrier fluid and $V_{\text{LS}}$ is the liquid superficial velocity. The output are the height $Z$ of the plant and consequently the total head $H_{\text{in}}$ and the mechanical power $W$ available at the hydraulic converter. Such calculus scheme has allowed to evaluate (along with plant sizes and performances) two particularly significant efficiencies as the thermodynamic one $\eta_t$ and the hydraulic one $\eta_{\text{hy}}$. The former is commonly given as the ratio between the thermodynamic cycle power $W_t$ (product of working fluid mass flow rate $G_w$ and the cycle work per unit mass $L_u$) and the inlet thermal power $(W_{i})$. The latter is the ratio between the mechanical power $W$ and $W_t$. It derives that the overall plant efficiency is given by $\eta_o = W / (W_{i}) = \eta_t * \eta_{\text{hy}}$.

3. RESULTS ANALYSIS

Geometrical characteristics and performances of thermogravimetric plants operating with water as carrier fluid, coupled with different types of working fluids, are reported in the present section. The following values have been fixed: minimum cycle temperature $T_{\text{min}} = 30 ^\circ\text{C}$, two-phase duct diameter $D_{\text{T-PD}} = 1000$ mm and liquid superficial velocity $V_{\text{LS}} = 1.2$ m/s. The curves of the plant height $Z$, power plant $W$ and hydraulic efficiency $\eta_{\text{hy}}$ versus $R$, for several values of the maximum cycle temperature $T_{\text{max}}$, are drawn in Fig. 3, 4, 5, respectively. The working fluid is the perfluorocarbon PF 5050 according to a saturated cycle (solid line of Fig. 2). From Figs. 3 and 4 it derives that $Z$ and $W$ increase when $R$ and $T_{\text{max}}$ increase. We can observe that power variations are larger than height changes: in particular, when $R$ varies between 0.01 and 0.03 and $T_{\text{max}} = 80 ^\circ\text{C}$, the plant height $Z$ increases around 20 % but the plant power augmentation is more than the double. The isothermal expansion 3-4 in the regenerated thermogravimetric system, corresponding to the adiabatic expansion in the Rankine cycle, allows to obtain a major work per unit mass $L_u$. Furthermore, a notable characteristic of the thermogravimetric cycle is the possibility of performing a significant regeneration. Yet, in the low enthalpy range, the difference between the extreme cycle temperatures simply amounts to a few tens of degrees and consequently, in the field investigated in the present work, the thermodynamic efficiency $\eta_t$ is no higher than 15 %. However, the thermodynamics of a regenerated thermogravimetric cycle is rather notable, when the irreversibility profile is taken into account. In such case, the second principle efficiency is around 90 % for saturated cycles and around 83 % for superheated cycles. As the hydraulic efficiency $\eta_{\text{hy}}$ (Fig. 5), it derives that it remarkably increases when $R$ decreases, reaching high values for low $R$. Once fixed $R$, $\eta_{\text{hy}}$ slightly increases when $T_{\text{max}}$ goes up. Several quantities contribute to such effect and the trend of the curves cannot be easily anticipated: real gas effect, the viscosity of the water (along with its surface tension and density) depending on the temperature, really affect the corresponding trends. We can conclude by observing that low $R$ values allow to obtain elevated hydraulic efficiencies $\eta_{\text{hy}}$ and not elevated plant heights $Z$ but they induce a plant power reduction: this one (R being fixed) could be increased by increasing the two fluids flow rates that is the ducts diameter. Analogous curves are reported in Figs. 6, 7, 8, for the above cited conditions, in the case of another perfluorocarbon, the PF 5040. Once fixed $R$ and $T_{\text{max}}$, the latter as the former, allows to operate with greater plant powers $W$ ($\cong 30 \%$) and higher $\eta_{\text{hy}}$ ($\cong 20 \%$), yet it must double its plant height $Z$. We can also notice that in the case of PF 5040, once fixed $R$, the difference of $\eta_{\text{hy}}$ values is rather low, when $T_{\text{max}}$ changes: furthermore, compared to the case of PF 5050, the trends of Fig. 8 are much more closed and the curve $T_{\text{max}} = 90 ^\circ\text{C}$...
**Fig. 3**

- **PF 5050**
- Saturated cycle
- $T_{\text{max}}: 90 \, ^\circ \text{C}$
- $T_{\text{max}}: 80 \, ^\circ \text{C}$
- $T_{\text{max}}: 70 \, ^\circ \text{C}$
- $T_{\text{min}}: 30 \, ^\circ \text{C}$
- $D_{\text{TPD}}: 1000 \, \text{mm}$
- $V_{\text{LS}}: 1.2 \, \text{m/s}$

**Fig. 4**

- **PF 5050**
- Saturated cycle
- $T_{\text{max}}: 90 \, ^\circ \text{C}$
- $T_{\text{max}}: 80 \, ^\circ \text{C}$
- $T_{\text{max}}: 70 \, ^\circ \text{C}$
- $T_{\text{min}}: 30 \, ^\circ \text{C}$
- $D_{\text{TPD}}: 1000 \, \text{mm}$
- $V_{\text{LS}}: 1.2 \, \text{m/s}$

**Fig. 5**

- **PF 5050**
- Saturated cycle
- $T_{\text{max}}: 90 \, ^\circ \text{C}$
- $T_{\text{max}}: 70 \, ^\circ \text{C}$
- $T_{\text{min}}: 30 \, ^\circ \text{C}$
- $D_{\text{TPD}}: 1000 \, \text{mm}$
- $V_{\text{LS}}: 1.2 \, \text{m/s}$
Fig. 6

Fig. 7

Fig. 8
(1) Saturated cycle. $T_{\text{max}}: 60 \, ^{\circ}\text{C}$
(2) Saturated cycle. $T_{\text{max}}: 70 \, ^{\circ}\text{C}$
(3) Superheated cycle. $T_v: 70 \, ^{\circ}\text{C}$ $T_{\text{max}}: 80 \, ^{\circ}\text{C}$
(4) Superheated cycle. $T_v: 70 \, ^{\circ}\text{C}$ $T_{\text{max}}: 90 \, ^{\circ}\text{C}$

$\eta_{\text{hy}}$
lies between those of 70 and 80 °C. All that is basically due to the working fluids thermophysical properties. When the hydrofluorocarbon HFC 134a is used, then the corresponding trends of $Z$, $W$, $\eta_{hy}$ versus $R$ are reported in Fig 9, 10, 11, respectively. Here the curves are drawn both for a saturated cycle and for a superheated cycle. As the saturated cycle, the curves reported for HFC 134a show trends analogous to the ones of PF 5050 and PF 5040. In addition, for HFC 134a, comparisons between a saturated and a superheated cycle can be made. Once fixed $\Delta p = p_{\text{max}} - p_{\text{min}}$ (i.e. $T_v$), the superheating extent will induce a mean density reduction in the two-phase flow column: it also affects the accelerative and frictional pressure drops as well as the phases slip ratio. All that will create a variation in the plant height (Fig. 9) and in the hydraulic efficiency (Fig. 11): it is also worth mentioning that the amount of such variation could be partially due to the use of the thermodynamic tables. In Fig. 12, $Z$ and $W$ versus $R$ are reported for different $T_{\text{max}}$ when the hydrofluorocarbon HFC 125 operates with a saturated cycle and Fig. 13 shows the corresponding $\eta_{hy}$ trends. The critical temperature $T_c$ of this fluid is rather low: 66.2 °C. We can notice that $Z$ curves are flattening when $R$ increases: yet, these values are definitely high (about 200 m when $T_{\text{max}} = 60$ °C) and they increase more than 10 % for an augmentation of $\Delta T_{\text{max}} = 5$ °C. For these reasons the possibility of working with a hypercritical cycle (short dashes lines of Fig. 2) has not been taken into account. By analysing the figures considered so far we can notice the solution water-PP 50 appears to result the most significant.
4. CONCLUSIONS AND FUTURE DEVELOPMENTS

The possibility of operating with water-PFC or water-HFC has been investigated: in such context, the couple water-PP 50 seems to be the most significant. However, we have to remark that also in this case a thermogravimetric system is characterised by low power density and relatively high plant heights. Furthermore, even if the hydraulic efficiency $\eta_{hy}$ can reach elevated values, the overall plant efficiency $\eta_o = \eta_t \eta_{hy}$ will be rather low: as the difference between the extreme cycle temperatures only amounts to some tens of degrees, the thermodynamic efficiency $\eta_t$ will be no higher than 15% with the consequence to heavily reduce $\eta_o$. However, as the characteristics of a thermogravimetric system are basically affected by the running fluids properties, it will be worth investigating new types of operating couples. In such sense we intend to examine the so-called “Fluoroinert” series characterised by fluids with a density up to 1.9 kg/dm$^3$ and a boiling point up to 200 °C.

REFERENCES