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H_2FC

Integrating European Infrastructure to support science and development of Hydrogen- and Fuel Cell Technologies towards European Strategy for Sustainable, Competitive and Secure Energy

Deliverable 8.7

D8.7 Test Rig for Steam Reformer Degradation Analysis

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Document History

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26.11.2013	1.0	Giovanni Cinti
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Introduction

The Deliverable 8.7 - Test Rig for Steam Reformer Degradation Analysis - is referred to the subtask JRA2.5.1 of WP8. The task title is “Test facilities for steam reforming”, described as follows:

- *The main focus of this task is the characterization of system degradation effects with respect to catalyst poisoning and stability of CO_2-sorbent characteristics in multi-cycle function. The goal is to improve a test setup for the analysis of materials characteristics and their stability according to suitable life cycle tests. The major impact expected is the possibility of sorption enhanced SMR and facility improvement to manage sorption-desorption cycles, also in presence of operating conditions variation according to scheduled life cycles*

Before the H2FC project, University of Perugia was not equipped with a test bench for degradation analysis of integrated catalyst-CO2 sorbent materials for sorption enhanced steam methane reforming (SE-SMR), able to guarantee:

- a wide range of temperature, pressure, gas feeding mixtures and flow rates conditions;

- test of solid materials in quantity form tens up to 100 gr.

Therefore, within subtask JRA2.5.1 the test rig prototype was completely designed and realized. The final validation was completed in December 2012 (M14). The deliverable was completed 100%.

In particular, after design of all technical specifications for both reactor and test bench (Section *Design*, points I.1 and I.2), beyond that definition of the procedure of experimental SE-SMR and sorbent regeneration tests (Section *Design*, point I.3), the designed equipment was acquired and set up at the beginning of November 2012. Subsequently, test bench functioning was successfully validated by means a suitable test campaign. All the activity complies the deadline indicated for deliverable D8.7.

It is highlighted that the results of the design activity is object of the paper “Innovative sorbents for SE-SR: Test bench and procedure” accepted for EFC 2013 (Fifth European Fuel Cell Technology & Applications Conference - Piero Lunghi Conference), while the experimental activity cited above is object of the paper “Synthesis and test of innovative sorbents based on calcium aluminates for SE-SR” submitted for publication to Applied Energy.

1 Design

1.1 Design of the SE-SMR reactor

The design of the reactor was performed according to the scheme of Figure 1. The geometry optimization was carried out by means of CFD modelling and simulations inclusive of the kinetics of all the occurring reactions, i.e. methane steam reforming, water gas shift and CO2 sorption through solid sorbents. Reactions kinetic modelling was carried out in reference to data available in literature relative to conventional materials (nickel as catalyst and calcium oxide as sorbent). The main result was the optimization of reactor geometry, e.g. determination of the optimal reactor length/diameter ratio (about 20). Moreover the reactor was sized in reference to an inner diameter Di=20mm.

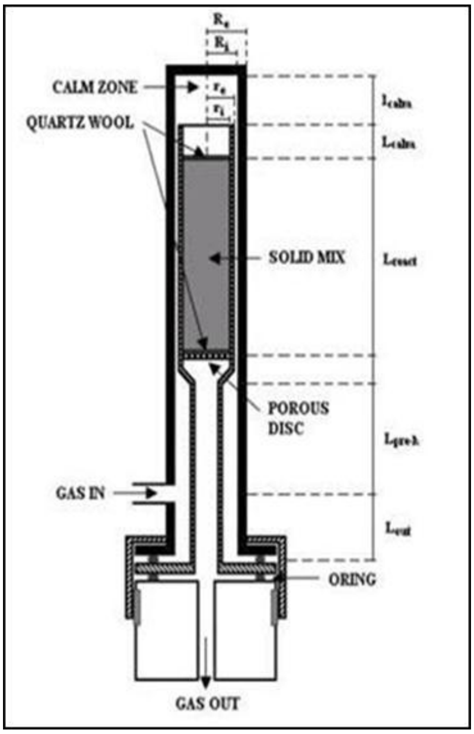


Figure 1 : SE-SMR Reactor scheme

1.2 Design of the test bench

Target of this activity was the bench design for the execution of SE-SMR tests, aiming to the evaluation of H2 production efficiency in function of the temperature and pressure operating conditions, the feeding gases mixture and the catalyst/sorbent weight ratio, beyond that their typology.

Only one fixed bed reactor (equipped with a pressurization system), according to point 1), was considered. In this reactor reforming/carbonization and sorbent regeneration processes are alternatively realized. The designed test bench guarantees operative conditions variable within 5-10 bar and 500-900°C, beyond that variable feeding mixture in terms of both flow rate and composition (CO2, N2, air, H2, CH4).

It is constituted of four main sections (Figure 2): gas feeding, water-vapor feeding, reactor, gas analysis. CO2 (max 0.21 NL/min), N2 (max 1.26 NL/min), Air (max 1.26 NL/min), H2 (max 1.26 NL/min), CH4 (0.21-0.42 NL/min) for reactor feeding are obtained from high purity gas cylinders, stored outside laboratory in a specific cylinders package, through suitable flow-meters interfaced with the data acquisition (DAQ) system. The laboratory is provided with a supply line of deionized water. Steam flow rate is variable in the range 0.42-0.84 NL /min, to allow the operation under different values of the S/C (steam to carbon) ratio. Liquid water is fed using a gear pump (regulation by means of a water flow rate control module interfaced to the DAQ system) and evaporated by a boiler. It is possible to vary the operational system pressure in the range 1-10 atm. Components incorporated in the test bench are the vaporizer and the deionized pressurization device. Pressure indicators, interfaced with the data acquisition system, are installed at the reactor inlet and outlet to monitor the system pressure; moreover a pressure relief valve is placed to protect reactor from excessive pressure. Reactor temperature is maintained by a split-tube furnace with integrated regulation (with the possibility to preset temperature ramps; the furnace temperature control module is interfaced to the DAQ system). Such a device can assure a constant (±5°C) temperature until 1200° C along the reactor length (heated length equal to the reaction zone of the reactor; compatible with maximum external reactor diameter of 38 mm).

Downstream of the fixed-bed reactor the product gases are sent to a gas analysis section. Such a section is composed by a gas chromatograph already available in the FCLab. All the sensors and actuators are interfaced to the DAQ and control system. The test bench described above is equipped with specific safety devices and located in the FCLab.

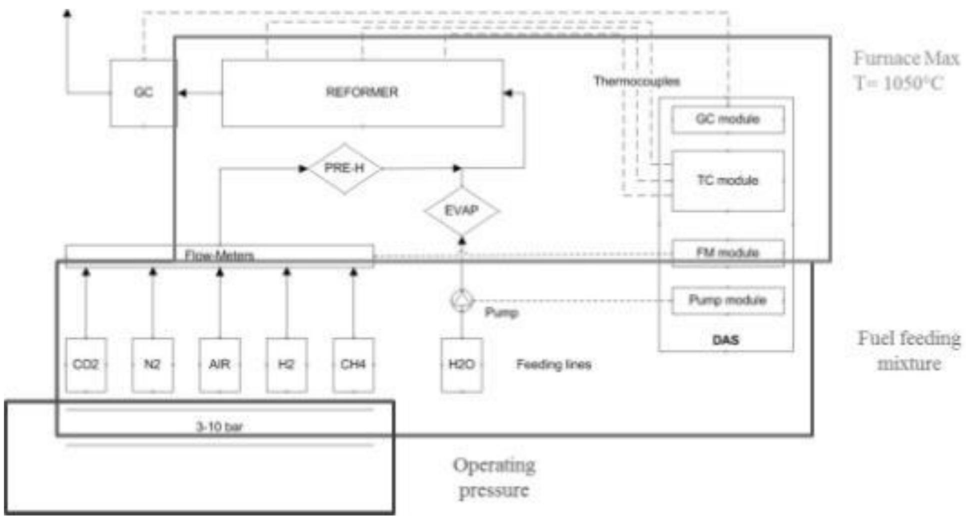


Figure 2: Test Bench layout

Finally, the specifications relative to the test bench control system were defined to allow the experimental procedure detailed in the next Section I.3. This to guarantee scheduling of multi-cycle tests, with each cycle made up of multiple phases characterized by different conditions, e.g. temperature, feeding gas composition and flow rate.

1.3 Definition of the procedure for the experimental tests

For the execution of SE-SMR tests, a suitable procedure has been determined. Such a procedure includes, for each test, 4 main steps: pre-calcination of the sorbent material, catalyst activation, hydrogen production process, sorbent regeneration.

At first, the sorbent material, mixed with the catalyst in particular weight ratio, will be pre-treated in air at the regeneration temperature and at ambient pressure to regenerate the sorbent; this phase will end when no CO_2 will be observed in the effluent gas. Before the reforming step, the reactor will be cooled down to the operational process temperature in H2/N2 atmosphere, increasing the pressure to operational value, to reduce the catalyst. Then the reactor feeding will be switched to the fuel composition gas and, by means of the gas chromatography section, the system performances in terms of hydrogen purity and methane conversion will be analyzed (the fluid-dynamic characterization of the solid bed will be carried out through suitable pressure sensors). At the end of the reforming step, the sorbent will be completely carbonated and it will be regenerated, in presence of the catalyst, through a regeneration process at the characteristic sorbent temperature and at ambient pressure. The gas regeneration composition is important because, if catalyst and sorbent are both exposed to an oxidizing atmosphere, the active catalyst would be re-oxidized during each regeneration cycle and would have to be re-reduced at the beginning of each cycle. The progress of the regeneration reaction is followed by monitoring the CO2 content in the product gas. A fixed quantity of H2 is injected into the product gas downstream of the reactor during CO2 regeneration, and regeneration will be complete when the H2 content of the product gas will become constant. During the execution of each test, at the end of each cycle of production/regeneration, the catalysis efficiency of the innovative catalysts will be estimated (also relative to the adsorption capacity of the sorbent), in reference to the operating conditions of the test in execution. In relation to sorbent material, during the experimental test, the decay of sorption capacity depending on the cycle’s number, regeneration process temperature and atmosphere in which regeneration will be estimated. Consequently, also the effect of the sorption capacity decay on the global performance of the SE-SMR process will be estimated. Within the experimentation, the variable parameters will be the catalyst and sorbent type, their weight ratio in the solid mix loaded in the reactor, operating temperature and pressure conditions of the reforming and calcination process and the feeding gas composition.

1.4 Test bench set up

The test rig was realized according to all detailed above. It was delivered in November 2012 and passed correctly the acceptance test. Figure 3 shows a picture of the test rig, after its installation in the FCLab. The synoptic scheme of the test bench, as it appears on its control panel, is depicted in Figure 4.

Figure 3: Picture of the test rig and transport documentation

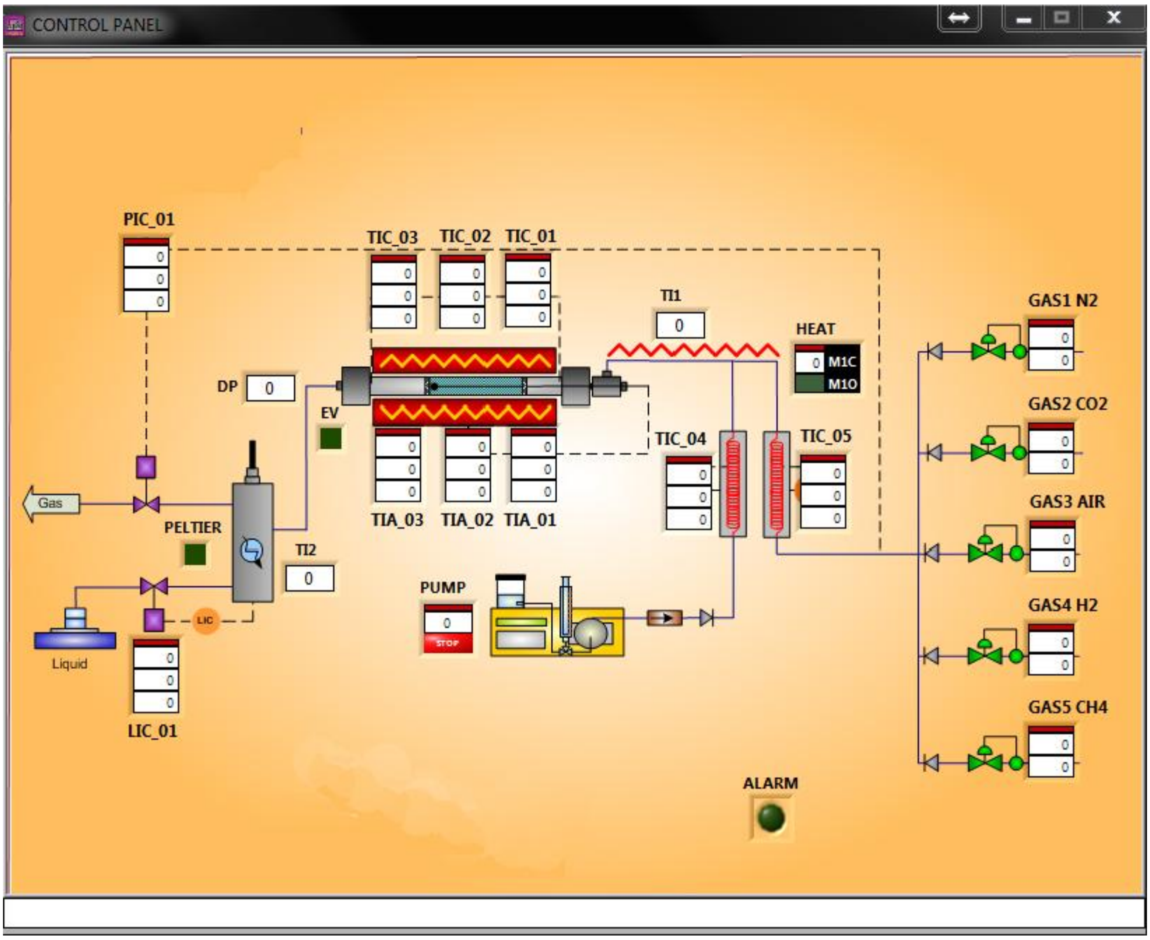


Figure 4: Test rig synoptic

2 Validation of the test bench functioning

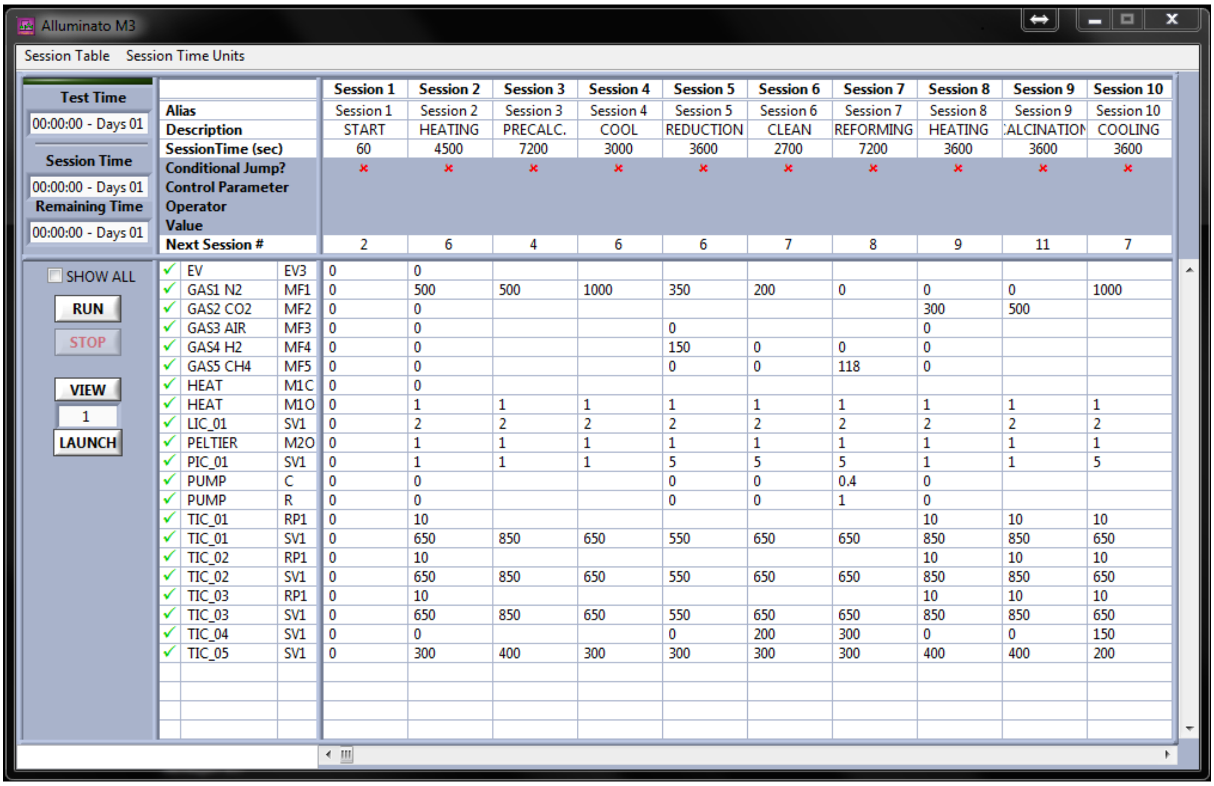
After the acceptance test, a wide range of test rig functionalities was validated through a suitable test campaign. The tested operating conditions are the ones fixed for the experimental performance evaluation of an innovative integrated catalyst-CO2 sorbent material for SE.SMR process. In particular, among the materials object of investigation and detailed in Section II.1, three different CO2 sorbents based on calcium aluminates were considered. In Section II.2 some results.

2.1 Definition of innovative typologies of catalysts and sorbents to be tested

Regarding materials typology, the solution with Ni-based catalyst and CaO-based sorbent has been chosen. In particular, sorbents obtained through CaO incorporation into inert material, that acts as structural support, has been chosen to improve sorption stability respect to conventional CaO. In particular, as inert materials SiO2, Al3O3 e TiO2 have been selected.

2.2 Results of the validation test campaign

In the first test campaign, carried out to validate test bench functionality, materials based on Ni-catalyst and calcium aluminates were tested in multi-cycles processes. Different operative temperatures in the reforming phase and the needed switch between reforming and calcination atmospheres and temperatures was realized. Figure 5 shows the session table filled up, within the test rig management software, for experimentation of material M3.



			Session 1	Session 2	Session 3	Session 4	Session 5	Session 6	Session 7	Session 8	Session 9	Session 10
Alias			Session 1	Session 2	Session 3	Session 4	Session 5	Session 6	Session 7	Session 8	Session 9	Session 10
Description			START	HEATING	PRECALC.	COOL	REDUCTION	CLEAN	REFORMING	HEATING	:ALCINATION	COOLING
SessionTime (sec)			60	4500	7200	3000	3600	2700	7200	3600	3600	3600
Conditional Jump?			×	×	×	×	×	×	×	×	×	×
Control Parameter												
Operator												
Value												
Next Session #			2	6	4	6	6	7	8	9	11	7
✓	EV	EV3	0	0								
✓	GAS1 N2	MF1	0	500	500	1000	350	200	0	0	0	1000
✓	GAS2 CO2	MF2	0	0						300	500	
✓	GAS3 AIR	MF3	0	0			0			0		
✓	GAS4 H2	MF4	0	0			150	0	0	0		
✓	GAS5 CH4	MF5	0	0			0	0	118	0		
✓	HEAT	M1C	0	0								
✓	HEAT	M1O	0	1	1	1	1	1	1	1	1	1
✓	LIC_01	SV1	0	2	2	2	2	2	2	2	2	2
✓	PELTIER	M2O	0	1	1	1	1	1	1	1	1	1
✓	PIC_01	SV1	0	1	1	1	5	5	5	1	1	5
✓	PUMP	C	0	0			0	0	0.4	0		
✓	PUMP	R	0	0			0	0	1	0		
✓	TIC_01	RP1	0	10						10	10	10
✓	TIC_01	SV1	0	650	850	650	550	650	650	850	850	650
✓	TIC_02	RP1	0	10						10	10	10
✓	TIC_02	SV1	0	650	850	650	550	650	650	850	850	650
✓	TIC_03	RP1	0	10						10	10	10
✓	TIC_03	SV1	0	650	850	650	550	650	650	850	850	650
✓	TIC_04	SV1	0	0			0	200	300	0	0	150
✓	TIC_05	SV1	0	300	400	300	300	300	300	400	400	200

Figure 5: session table scheduling

All the characteristic of the investigated materials and related detailed results, are discussed in the paper "Synthesis and test of innovative sorbents based on calcium aluminates for SE-SR" submitted for publication to Applied Energy.

As example, Figure 6 summarizes main results obtained for material M3 varying reforming operative temperature, relative the reforming phase. Moreover, Figure 7 depicts CO2 sorption capacity of materials M1 and M3 in multi-cycle tests.

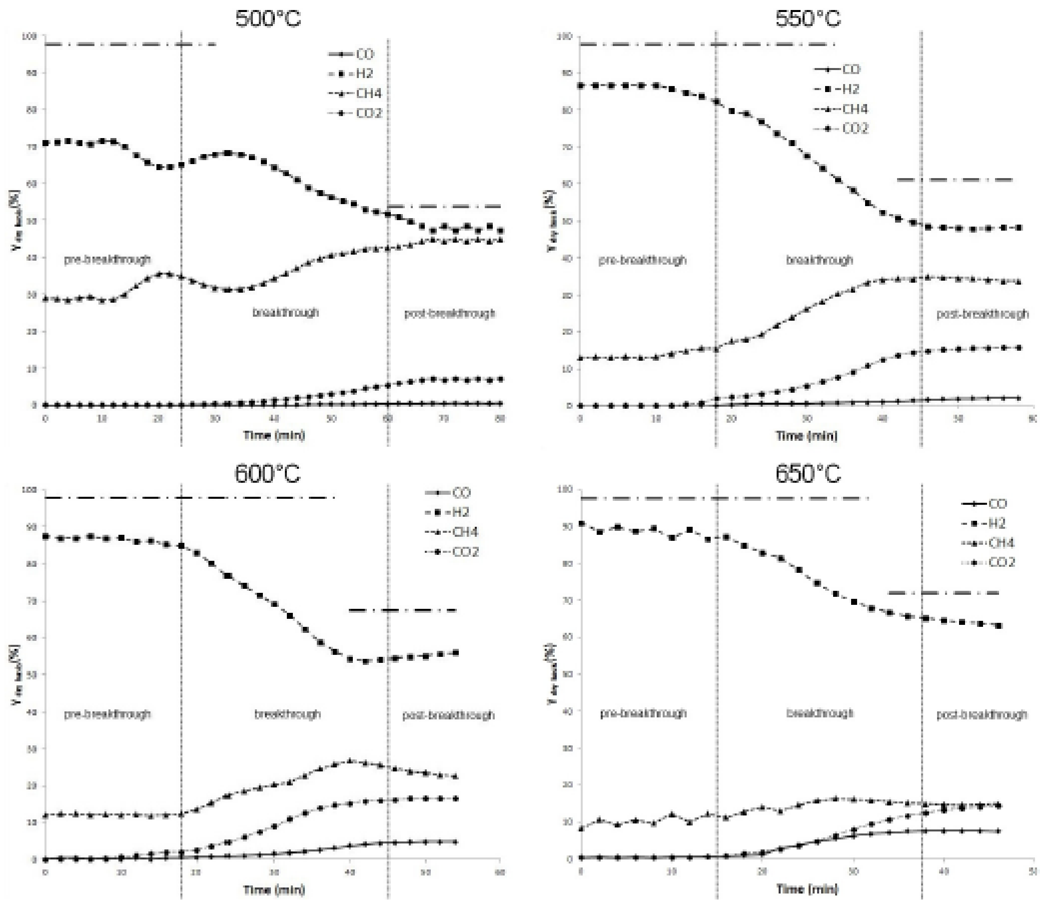


Figure 6: reformate gas composition at different operative temperatures (material M3)

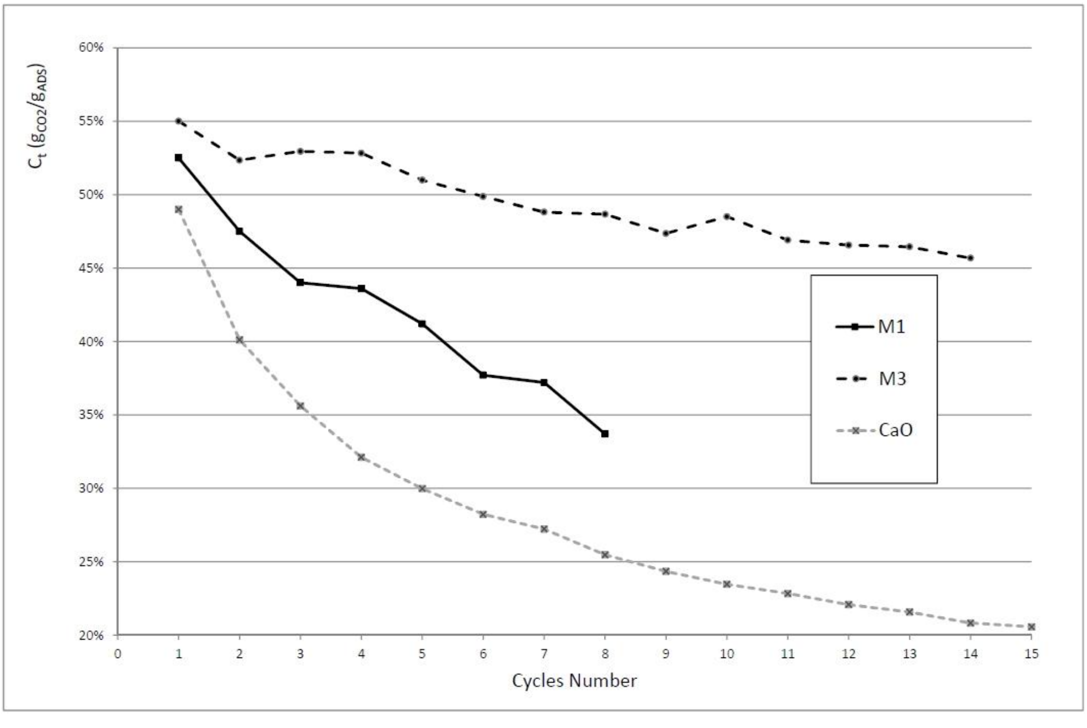


Figure 7: CO2 sorption capacity in multi-cycle tests of materials M1 and M3

Conclusions

The test rig was delivered in November 2012 and passed correctly the acceptance test. The preliminary positive results, on innovative synthesized materials, came from the test rig in December 2012. Part of the results are object of the article "Synthesis and test of innovative sorbents based on calcium aluminates for SE-SR" submitted for publication to Applied Energy.

The obtained results demonstrated the test rig well-functioning and its potentials, i.e.:

- variable solid load from tens up to 100 gr
- variable operative temperature up to 900°C
- variable pressure up to 10 bar
- variable feeding gas composition (as mixture of CO2, N2, air, H2, CH4) and flow rates (up to 1000 ml/min)
- scheduling of multi-cycle tests, with multi-phase cycles (in each phase it is possible to set different conditions for the parameters cited above).

In particular it is highlighted, respect to the state of the art, the possibility to operate, at the same time, at high pressure and high temperature. To this aim a Hastelloy X reactor and other technological solutions were considered in the test rig design and realization.