INNOVATIVE PASSIVE PROTECTION SYSTEMS FOR HYDROGEN PRODUCTION PLANTS

Cercignani, G., Cozzani, V., Nicolella, C. and Zanelli, S.
Dipartimento di Ingegneria Chimica-Chimica Industriale-Scienza dei Materiali, Università di Pisa, Via Diotisalvi N°2, Pisa, 56126, Italy

ABSTRACT

As a part of a broader project on hydrogen production by reforming of methane in a membrane catalytic reactor, this paper outlines the research activity performed at the University of Pisa, Department of Chemical Engineering, aimed at developing and testing composite panels that can operate as thermal protective shields against hydrogen jet fires. The shield design criterion that appears to give a more practical and convenient solution for the type of installation to be protected, is the one that suggest to realize composite panels. Composite material are made of two elements, fiber and matrix. In this study, composite panels will be realized with basalt fabric as fiber and epoxy-phenolic resins as matrix. Therefore, following the indications given by norms as UNI 9174 and ASTM E 1321-93, a test method has been studied to obtain temperature data from a specimen impinged by an hydrogen flame. Thanks to thermocouples applied on backside of the sample and an infrared video camera to realize thermal images of specimen surface impinged by flame, this type of test try to characterize the behaviour of composite materials under the action of hydrogen flame, simulating, in a simple way, the action of hydrogen jet fires.

1.0 INTRODUCTION

With the purpose to realize passive protection systems useful to protect plants against jet fires due to accidental leakage of hydrogen, a research in literature has been made to find the principal methods used in industries. Thermal shields can be realized following different criteria:

1. the heat is absorbed by a sufficient mass of material, that will be heated up to a temperature close to the melting point. Materials such as copper, aluminium, magnesium e tungsten are used for this application. However, the use of these shields s is not practical for passive protection against hydrogen jet fire.

2. the surface, impinged by the flame, could be protect by a cover of self-extinguishing materials, which are also able to irradiate heat back and to partially absorb it with an ablative mechanism. Self-extinguishing resins are able to resist direct flame for determined time interval.

3. the heat could be removed from surfaces impinged by flame by covering them materials which decompose, fuse or vaporize under the action of the fire heating. Such a type of ablative mechanism is able to remove a very great amount of heat. However it is necessary to find a filling material that permit to realize solid structures, useful to support shield also after the “fire treatment”.

The third shield design criterion appears to give a more practical and convenient solution for the type of installation to be protected, so the attention has been concentrated on the possibility to realize panels made with composite materials suitable to support strict exercise conditions imposed by the incidental scenario mentioned above. To verify fire and heat resistance characteristics of these panels, they will be subjected to tests adapted from those codified and reported by UNI and ASTM standards. As a part of a broader project on hydrogen production by reforming of methane in a membrane catalytic reactor, this paper outlines the research activity performed at the University of Pisa, Department of Chemical Engineering, aimed at developing and testing composite panels that can operate as thermal protective shields against hydrogen jet fires.

2.0 MATERIALS

Modern composites are generally made with two basilar components, a fiber and a matrix. Fiber is often glass, but sometimes may be Kevlar, carbon fiber or polyethylene. Matrixes usually have a thermosetting composition like epoxy resins, polydicyclopentadiene or polyimide. Fibers are put in a matrix to increase their resistance.

For the above mentioned application, fabrics obtained from basalt filaments will be the fiber in composite panels. As shown in table 1, they present, at comparable cost, better thermal properties than conventional glass fibers. They offer lower performances than silica filaments, which, on the other hand are more expensive.

This type of fiber is directly produced using basalt rocks or rocks containing this mineral. It has a detached alkaline property, due to the type of magma that originates the basalt. Typical rock composition for production of these filaments is shown in table 2.2.

It is very important to find a suitable matrix to complete composite panel; according to the type of use, different matrixes can be taken in consideration. There are cheap matrices with acceptable properties, e.g. unsaturated systems made with polyester/styrene. They are useful for common applications.

Table 1. Thermal properties of some kind of fiber.

Thermal Properties	SI Units	Basalt Filaments	Fiberglass	Silica Filaments
Maximum application temperature	(°C)	982°	650°	1100°
Sustained operating temperature	(°C)	820°	480°	1000°
Minimum operating temperature	(°C)	-260°	-60	-170°
Thermal conductivity	(W/m K)	0.031-0.038	0.034-0.04	0.035-0.04
Melting temperature	(°C)	1450°	1120°	1550°
Vitrification conductivity	(°C)	1050°	600°	1300°-1670°
Glow loss	(%)	1.91	0.32	1.75
Thermal expansion coefficient	(ppm/ °C)	8.0°	5.4°	0.05°
Price Comparison		$	$	$$$$

Table 2. Typical rock composition to produce basalt filaments (%).

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	K_2O	Na_2O	MgO	CaO	MnO	P_2O_5
50.2 - 47.5	2.0 - 0.7	18.6 - 15.1	14.8 - 11.7		7.5 - 2.6	3.3 – 2.3	6.7 - 4.8	12 - 6	—	—

Another cheap system is the so called vinyl ester resin. To obtain vinyl ester resin a diepoxide must react with acrylic acid or metacrylic acid (Figure 1).

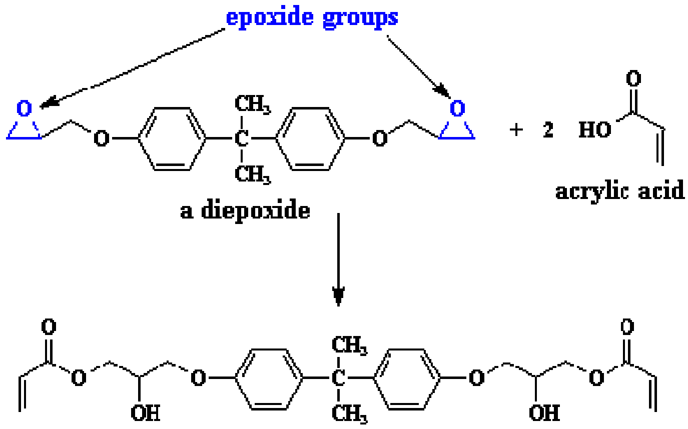


Figure 1. Reaction between diepoxide and acrylic acid

Then vinyl groups polymerise and a reticulated resin can be obtained. Sometimes greater oligomers, like that shown in Figure 2, can be used.

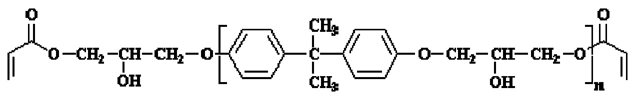


Figure 2. Example of greater oligomer.

Neither vinyl ester or unsaturated polyester are suitable for applications at high temperature. For high temperature it is necessary to use matrices made with epoxy resins, obtained by reticulating a diepoxide a diamine. Epoxy groups react with diamine and the entire system become reticulated (Figure 3):

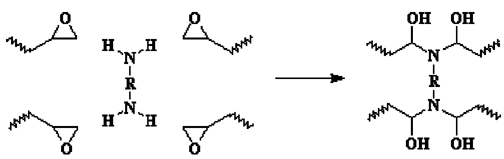


Figure 3. Reaction between epoxy groups and diamine

Due to the presence hydroxyl groups, epoxy resins bind themselves to glass fiber. They have some properties that are not found in other matrices: they do not absorb water, they do not shrink themselves when they are reticulated and they can be used at high temperature. Moreover there are other possibilities for applications at high temperature. Polyimide resist at very high temperature, but they absorb al lot of water, so this event cause break of material. Polybenzoxazolide also resist at high temperature but it's impossible to process them. Some researches are made to develop hydrocarbon matrices.

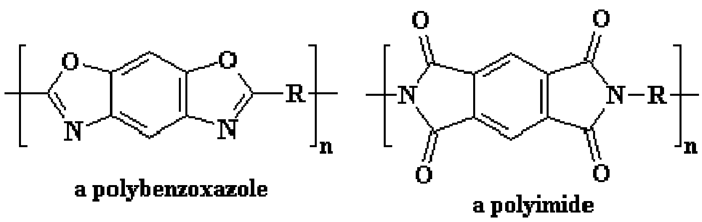


Figure 4. Examples of other resins

Other types of resin particularly resistant at high temperature are made with phenolic or epoxy-phenolic components. A very interesting property is the ablative mechanism that phenolic and epoxy resins, opportunely additivated, can present. Such matrices do not fuse when they are invested by the flame, but they generate gaseous products of decomposition that cool the material, diffusing through the superficial carbon layer, formed in the first moments of operation, removing, in this way, a great amount of heat.

Therefore the idea is to realize composite panels made with fabrics of basalt fiber impregnated with a epoxy-phenolic resin. With the purpose to increase the performances of like-made panels, self-extinguishing resins or varnishes (usually constituted by halogenated compound) can be used to cover panel surface so as to raise composite structure capacity of resistance to flame; another possibility could be to use intumescent materials, such as cement or filler, to give rigid structure to panel, but also to promote absorption of heat produced by jet fire.

3.0 NORMS AND FIRE RESISTANCE TESTS

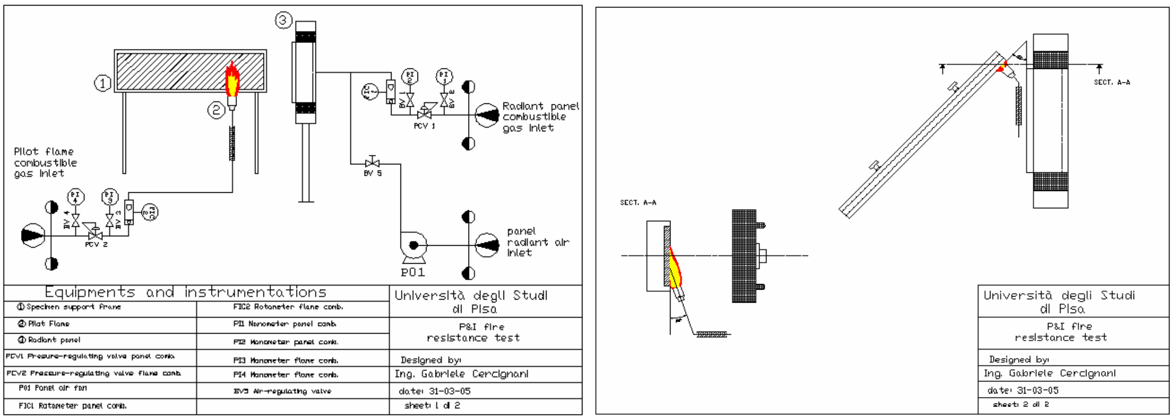
When one or more resins, considered compatible with basalt fibers and suitable to resist at exercise conditions imposed during hydrogen jet fire, are selected, it’s important to test and estimate the effective performances of composite material, and to define its characteristics of flame and heat resistance.

With the purpose to carry out these tests, some research centres and sets of rules suggest various methods suitable to assess thermal and mechanical properties of materials subjected to the action of fire. In particular, to estimate reaction to fire a material can be hit by pilot flame with radiant heating, ministerial decree on date 26-09-1984, dawned with ministerial decree on date 03-09-2001, suggest to follow indications given by norm UNI 9174-9174/A1.

Also ASTM norms provide test methods like those described in UNI norms. In particular ASTM norm E 1321-93 present a similar test to assess ignition and flame front diffusion characteristics of materials subjected to a flame with radiant heating. These types of test allow the estimation of the behaviour that the panel can present when it is impinged by a pilot flame, in presence of radiant heating, and the evaluation of the minimum thermal surface flux and time for ignition, velocity of lateral flame spread along the sample surface. It is also possible to define parameters important to compare different materials, such as effective material inertia value ($k\rho c$) and flame-heating parameter pertinent to lateral flame spread (Φ).

In Figures 5 a) and b), P&I of the test type suggested by norms is presented to better understand procedures and equipments involved. As it can be observed, the system comprises two main components: i) the framework, that includes the specimen support frame, on which the composite material sample will be fixed; ii) the set of equipments that constitute the radiant panel.

The bearing structure on the first component is realized by stainless steel, covered by epoxy varnish, and the specimen support frame, fixed to the structure, is made with the same material and has dimensions suitable to hold 155 x 800 mm sized material samples, with variable thickness. The blocking system is realized with screws able to put the specimen against the edge made on the specimen support frame.



a) b)

Figure 5 a) and b). P&I e orientation of equipments for the test suggested by norm.

The second element is constituted by a radiant panel made with porous refractory material of dimensions 300 x 450 mm and by its combustible gas feeding system.

In adding to these two elements, norms provide for the use of a nozzle burner to realize a maximum 120mm length pilot flame, placed to have an angle of 20° regarding the specimen surface; therefore the experimental equipment have a second line of combustible gas feeding.

However this type of test don't simulate in satisfactory way all the effects that in reality a jet fire, impinging on the surface of protective panel, can produce. For this reason some modifications have been made to procedure and equipments of the test suggested by norms.

4.0 DESIGN OF EXPERIMENTAL TEST

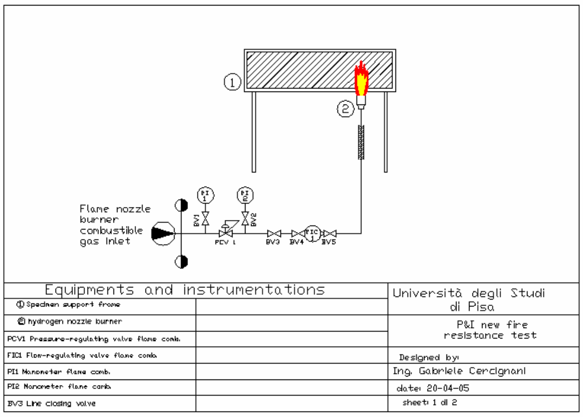
With the purpose to realize a type of test suitable to obtain data useful to analyse the behaviour of protective panels subjected to the action of jet fires, procedure and equipments provided by norms have been modified.

The bearing structure, that must support the specimen and the dimensions of the specimen (155 x 800 mm), that must be subjected to the action of flame, remain the same as suggested by norms. The main modification consists in not using the radiant panel as heating system, so that its bearing structure and its feeding system are no more necessary; instead of the radiant panel, the heating source is the flame produced by a nozzle burner for hydrogen.

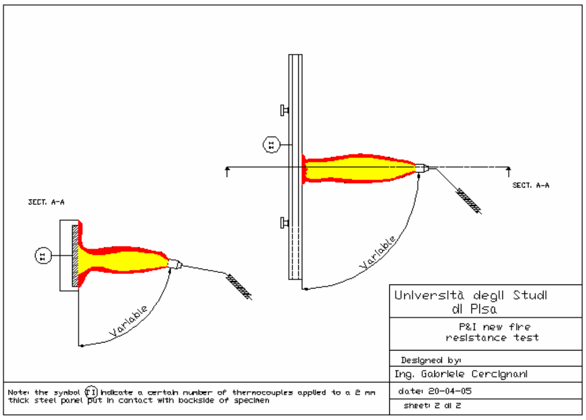
This nozzle burner produces a diffusion flame with a length included between 300 mm and 800 mm and with maximum diameter of 70 mm. It is mounted on a bearing structure that allows the variation in all directions of the flame/sample impact angle. Therefore the nozzle burner is supplied with a combustible gas feeding line, covered with insulation material to protect it by heating. The gas feeding line is constituted by: a hydrogen cylinder (hydrogen), a pressure-regulating valve with two manometers to control pressure upstream and downstream the pressure-regulating valve, a valve to close the line, tube and flow regulator chosen according to exercise conditions and flow rate of hydrogen.

The instrumentations, used to collect data useful to understand the behaviour of tested materials, are: an infrared video camera, that allow the control of constant temperature of sample surface, impinged by the flame; a certain number of thermocouples type K (Chromel/Alumen) fixed to a 2 mm thick steel panel, put in contact with the backside of specimen and used to analyse the variations of time/temperature on the specimen; a data acquisition system (data logger) with analogical and digital signal ports to interface thermocouples with a computer and a video board to acquire images provided by video camera.

In the figures 6 a) and b), the new configuration of the fire resistance test and an example of infrared video camera for thermal images can be seen.



a)



b)

Figure 6 a) and b). P&I and equipments orientation of new test configuration.

Figure 7. Example of infrared video camera.

However the interpretation of acquired data is under evaluation, as it is important to understand the meaning of data obtained by thermocouples and video camera, and how much this type of test is near to the real effects of a jet fire impinging protective composite panels.