

# Evaluation of thermodynamic properties of concrete substrates and cement slurries modified with admixtures

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## ABSTRACT

The study of the creation and the stability of the interface between concrete substrates and repair systems needs the knowledge of the thermodynamic properties of materials. The measurement of the surface free energies of liquids is realised by means of Wilhelmy plate method on reference liquid and repair products. In order to determine polar and dispersive components, it is necessary to measure the contact angle of these liquids and products on reference solid surfaces and on concrete, mortars and aggregates.

Centrifuged solutions of repair product systems elements were prepared in order to measure surface free energies on pure liquids without solid particles in suspension. Evolution of properties versus time were also taken into account and analysed in comparison with well-known liquids and products.

## RÉSUMÉ

L'étude de la stabilité de l'interface entre un support en béton et un système de réparation nécessite la connaissance des propriétés thermodynamiques des matériaux. La mesure des énergies libres de surface des liquides est réalisée au moyen de la plaque de Wilhelmy sur des liquides de référence et des produits de réparation. Dans le but de déterminer les composantes polaires et dispersives de ces produits, il est nécessaire de mesurer les angles de contact que font ces liquides et produits sur des surfaces solides de référence.

Des solutions centrifugées de produits intervenant dans les systèmes de réparation ont été préparées afin de mesurer les énergies libres de surface des liquides purs, en l'absence de particules solides en suspension. L'évolution de ces propriétés avec le temps est aussi prise en compte et analysée en comparaison avec des produits liquides et solides bien connus. Des conclusions sont tirées quant à l'utilité et la qualité de ces mesures pour la prédiction du comportement des matériaux durcis.

## 1. INTRODUCTION

Repair works quality is depending on a lot of factors dealing with properties of the repair materials, the surface preparation of the substrate, the environment and the worker's qualification.

First of all however, it is important to verify the physico-chemical compatibility of concrete substrate and repair materials. As a slurry is often used to promote adhesion, this material was chosen to analyse the creation and the stability of the interface created between repair materials and concrete substrate.

Surface analysis, in conjunction with surface science and applied science is a major activity contributing to the knowledge of interfacial phenomena and, more generally, to our daily well-being through improvements in health, consumer products, environment, ... [12].

But we have to define exactly what we mean by "surface analysis". In its simplest sense, we require analysis of the elemental composition of the outermost atom layer of a solid. Having defined that, the next request will be for detailed knowledge of the chemical binding state, precise sites of atoms in relation to crystal structure, surface homogeneity and the state of adsorbates.

Surface free energy is a direct measurement of intermolecular forces. The free energy in surface layer is the result of the attraction of the bulk material for the surface layer and this attraction tends to reduce the number of molecules in the surface region resulting in an increase of intermolecular distance (Fig. 1). This increase requires work to be done and returns work to the system upon a return to a normal configuration: this explains why free energy exists and why there is a surface free energy.

The most common type of physical attractive forces

Editorial Note

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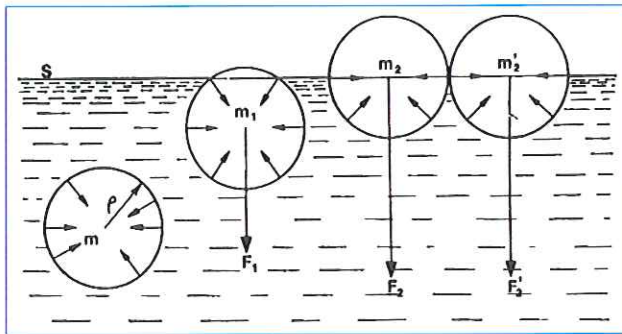


Fig. 1 – Relative attraction of molecules in bulk and surface [15].

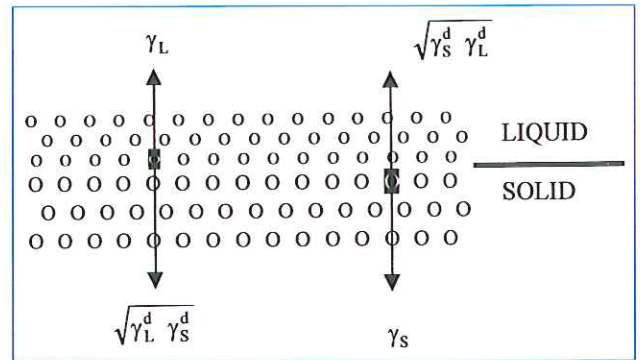


Fig. 3 – Dispersive forces at the interface solid/liquid [2].

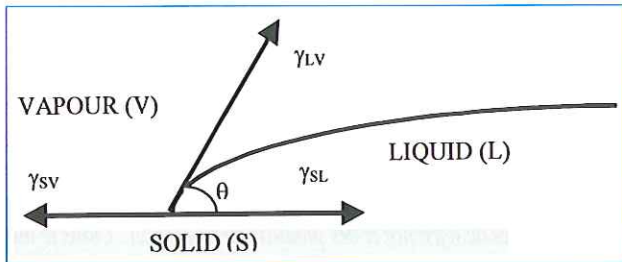


Fig. 2 – Wetting conditions of a solid by a liquid.

are the Van der Waals forces, and they can be attributed to different effects [4] :

- (a) dispersion forces arising from internal electron motions which are independent of dipole moments;
- (b) polar forces arising from the orientation of permanent electric dipoles and the induction effect of permanent dipoles on polarisable molecules.

Based on the thermodynamic equilibrium between a liquid drop and the solid surface, the analysis and the determination of the contact angle and the surface free energy of liquids let us to evaluate the respective effect of polar and dispersion forces.

## 2. PRINCIPLES FOR THE DETERMINATION OF SURFACE FREE ENERGY OF SOLID

The contact (Fig. 2) between the adhesive and the solid - in our case cement slurry, impregnation layer, resin, PC mortar, PCC mortar,... and concrete support - is the result of the wetting procedure [3]. Relation between contact angle and free energies of liquid and solid is described with the equation of Young and Dupre:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1)$$

with  $\gamma_{SV}$  = surface energy of solid/vapour  
 $\gamma_{LV}$  = surface energy of liquid/vapour  
 $\gamma_{SL}$  = interfacial energy solid/liquid.

The wetting procedure can be explained as follows [3]: the surface energies of the solid and the liquid interact each other and a change of the energy conditions occurs due to surface decrease of liquid/vapour and solid/vapour interfaces while new interface (liquid/solid) is created.

The interfacial energy is a residual of the initial surface energies that were not equilibrated. This interfacial energy (Fig. 3), as well as surface energies of liquid and solid, can be specified in two terms relatively to polar ( $\gamma^P$ ) and dispersive ( $\gamma^d$ ) interactions [1, 4].

The surface free energy into the liquid will be evaluated by the surface free energy of the liquid, restricted by a particular value due to the contribution of dispersive and polar forces of the solid.

Owens and Wendt [5] gave the definition of  $\gamma_{SL}$  as the geometric mean between these two effects:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} - 2(\gamma_S^p \cdot \gamma_L^p)^{1/2} \quad (2)$$

By combination with the equation of Young and Dupre (Equation (1)) and working with reference liquids and solids, it is possible to determine the polar and dispersive component of a solid from the next equation and the measurement of contact angle of these liquid on solid support:

$$1 + \cos \theta = \frac{2}{\gamma_L} \left[ (\gamma_S^d \cdot \gamma_L^d)^{1/2} + (\gamma_S^p \cdot \gamma_L^p)^{1/2} \right] \quad (3)$$

To know and evaluate the interactions at the interface, it is necessary to determine values of  $\gamma_L$ ,  $\gamma_L^d$ ,  $\gamma_L^p$  and  $\gamma_S$ ,  $\gamma_S^d$ ,  $\gamma_S^p$  and finally  $\gamma_{SL}$ .

Surface free energy of liquid is evaluated with the Wilhelmy balance ( $\gamma_L$ ). Contact angles are determined with a goniometer. The work program for the evaluation of dispersion and polar components of  $\gamma_L$  and  $\gamma_S$  is explained hereafter [2, 11]:

- we consider the surface free energy of a liquid X only determined by dispersion forces ( $\gamma_L^d$ );
- we choose reference solids where surface free energy is only determined by dispersion forces ( $\gamma_S^d$ );
- by measuring contact angles of determined liquids ( $\gamma_L$  well-known) on reference solids, we are able to determine the dispersion and, by subtraction, the polar component of surface energy of these liquids;
- by measuring contact angles of liquids on solids to be analysed, the two components of  $\gamma_S$  can be evaluated.

### 3. EXPERIMENTAL INVESTIGATIONS

#### 3.1 Preparation of cement slurries modified with admixtures

The penetration of repair system (coating, PC, PCC or CC, impregnation layer,...) is in relation with thermodynamic properties of liquids and solids but also with the granulometry of surface pores ( $r_p$ ) and viscosity of liquids ( $\eta$ ). In order to decrease the shear level ( $\tau_m$ ) and the viscosity ( $\eta$ ) of the slurries used to act as impregnation and bonding layer between concrete support and CC or PCC repair mortars, we used different types of admixtures (Table 1).

The liquid phase used for surface energies of liquids and solids determination was obtained according to the next procedure:

- mixing of water and cement CEM I 42.5 (W/C = 0.5) for 3 minutes and dividing in 4 parts to fulfil the containers of Sorval centrifugation device;
- centrifuging for 20 minutes at 6000 rounds per min;
- collecting the centrifuged solutions ( $\pm 100$  ml) into containers closed after filtration with Wathman paper nr 51 (retention of 20–25  $\mu\text{m}$  particles).

It is mainly this part of the slurries that will be able to penetrate the superficial porosity of concrete due to the relative dimension of cement particles and pore radius; in order to analyse thermodynamic equilibrium at the interface and wetting of concrete by cement slurries (modified or not), the use of centrifuged solutions seems to be more connected to real phenomena and to avoid interactive effect of viscosity on contact angle variation.

#### 3.2 Surface free energy of liquids

The determination of surface energy of liquids can be realised with Wilhelmy plate (Fig. 4) and tensiometer is based on the measurement of the weight necessary to pull out the metallic plate from the liquid to analyse.

Table 2 presents results of surface free energy of distilled water and centrifuged solutions of cement slurries. Only solution D seems to induce a significant modification of surface free energy.

Four different products (pure chemical products) were used as reference liquids while  $\alpha$ -bromonaphthalen is a chemical substance where only dispersion forces are able to interact  $\gamma_L = \gamma_L^d$ . This liquid will permit to determine dispersion component of solid surface.

#### 3.3 Surface free energy of solids

This work is realised by determining the value of contact angle of reference liquids (with well-known and non variable surface energies) with a goniometer (Fig. 5). Due to the heterogeneity of concrete, the measurement was

Reference	Admixture type	Shear strength of slurry (N/mm <sup>2</sup> )	Viscosity of slurry (mPa.s)	Viscosity of centrifuged slurry (mPa.s)
A	Melamine (macromolecules)	11.4	309	1.412
B	Melamine	8.35	670	1.463
C	Naphtalen	8.85	434	1.587
D	Vinyl copolymer	6.21	474	1.464
E	Maleic acid	14.15	486	1.366
F	Natrium ligno-sulfonate	21.66	1186	1.389
G	(no admixture)	32.75	1389	1.518

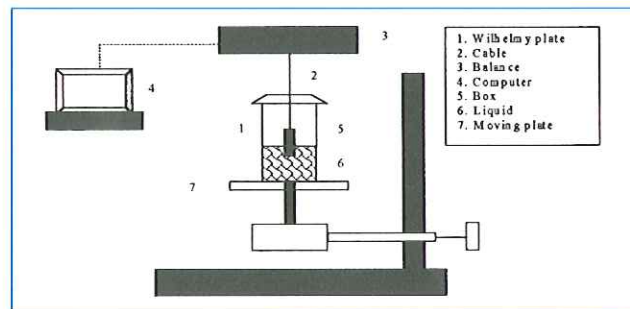


Fig. 4 – Wilhelmy plate tensiometer.

Reference	Temperature (°C)	Surface free energy (mN/m)
Distilled water	23.2	71.1
A	23.5	66.3
B	23.3	70.3
C	23.2	67.3
D	23.3	49.1
E	23.2	67.8
F	23.3	66.3
G	23.3	70.6
Dimethylformamide	23.1	36.3
2-dimethylethanolamine	22.9	27.95
3-dimethylamino-1,2-propanediol	22.8	36.1
Tetramethylen sulfone	23	49.6
$\alpha$ -bromonaphthalen	23.1	42.5

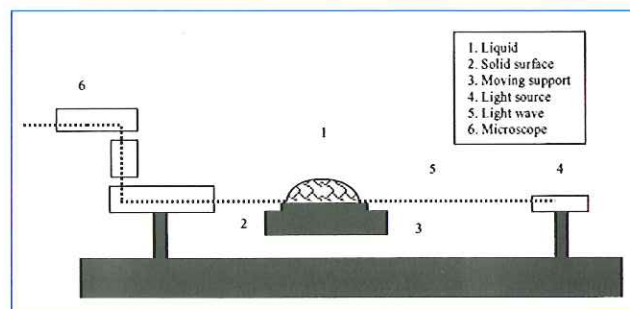


Fig. 5 – Measurement of contact angle of liquids onto a solid surface.

**Table 3 – Evolution of contact angle on a cement paste and limestone rock for reference liquids, water and centrifuged solutions of cement slurries modified with different admixtures versus time**

Reference	Cement paste		Cement paste + hydrophobic treatment		Limestone	
	20 sec.	2 min.	20 sec.	2 min.	20 sec.	2 min.
A	12	9	115	113	16	11
B	17	14	126	123	19	13
C	19	15	130	129	23	17
D	21	18	122	120	21	16
E	32	29	111	110	23	18
F	23	21	127	125	29	20
G	34	31	124	120	21	26
Distilled water	58	50	120	116	43	35
Dimethylformamide	22	-	49	-	0	-
2-dimethylethanolamine	22	-	0	-	0	-
Tetramethylen sulfone	59	-	112	-	21	-
α-bromonaphtalen	11	-	66	-	0	-

realised separately of the mortar part and the aggregate part.

Three main supports were tested :

- cement paste W/C = 0.4<sup>1</sup>
- cement paste W/C = 0.4 + hydrophobic treatment;
- limestone screwed rock.

Hydrophobic treatment was realised by application of DYNASYLAN BSM 100W (≈ 144 g/m<sup>2</sup>). Evolution of contact angle versus time is taken into account by measuring contact angle at different time steps.

Table 3 presents the results of contact angles measurements. For the contact phenomenon study, it is preferable to take into account instant values of contact angle because it is not significantly influenced by capillary absorption or roughness. However, if the rule is to investigate the suction properties, it is probably better to use values after 1 or 2 minutes.

The results hereafter are coming from more than 5 contact angle measurements in each situation.

A statistical treatment, based on multivariate variance analysis, was realised with contact angle as dependent variable and time, type of support and type of liquid as independent variable. The conclusions were:

- time has a significant effect on contact angle values;
- substrate has a significant effect on contact angle values. It is quite significant and evident for support with hydrophobic treatment;
- reference liquid has a significant effect on contact angle values.

<sup>1</sup> similar to the composition of the concrete (limestone aggregates 2/8, sand 0/2, cement CEM II B-M 32.5 (280 kg/m<sup>3</sup>) and water (W/C = 0.4)).

Many authors [4] already reported this time-temperature dependence. Influences of support and liquid are reasonably expected.

### 3.4 Determination of dispersion and polar components of liquids and solids

Parafilm (American Car Company) is a plastic polyethylene film [9] characterised by a polar component of its surface free energy equal to zero. If we use α-bromonaphtalen (γ<sub>L</sub><sup>P</sup> = 0), we shall be able to deduce from Equation (3) the value of γ<sub>S</sub><sup>d</sup> (Equation (4)):

$$\gamma_S^d = \frac{(\cos \theta_{\text{brom}} + 1)^2}{4} \gamma_{\text{brom}} \quad (4)$$

Measurements we have realised give a value of γ<sub>S</sub><sup>d</sup> = 38.15 mN/m, in accordance with literature [9].

The determination of contact angles of different liquids with Parafilm (Table 4) will permit to calculate the dispersion component of the surface free energy of these liquids because there is no polar possible interaction. By subtracting this value to γ<sub>L</sub> previously determined, it is possible for each liquid to evaluate γ<sub>L</sub><sup>P</sup>.

Calculation of dispersion component of liquid is so coming from Equation (3) where γ<sub>S</sub><sup>P</sup> = 0 (Equation (5)):

$$\gamma_L^d = \frac{1}{\gamma_S^d} \left( \frac{(1 + \cos \theta)}{2} \cdot \gamma_L \right)^2 \quad (5)$$

A similar development can be set up to calculate dispersion and polar components of solids. From the equation of Owens and Wendt (Equation (3)), it is possible to determine, by linear regression, the rate and the value at the origin for equation:

**Table 4 – Contact angles on reference solid and dispersion and polar component of liquids**

Reference	Contact angle on Parafilm (degree)	Dispersion component γ <sub>L</sub> <sup>d</sup> (mN/m)	Surface free energy γ <sub>L</sub> (mN/m)	Polar component γ <sub>L</sub> <sup>P</sup> (mN/m)
Distilled water <sup>1</sup>	101	21.7	71.1	49.4
Dimethylformamide	52	22.5	36.3	13.8
Tetramethylen sulfone	71	28.3	49.6	21.3
2-dimethylethanolamine	35	16.9	27.95	11.05
3-dimethylamino-1,2-propanediol	64	17.7	36.1	18.4
A	98	21.35	66.3	44.95
B	100	22.1	70.3	48.2
C	94	25.7	67.3	41.6
D	94	13.7	49.1	35.4
E	99	21.4	67.8	46.4
F	100	19.7	66.3	46.6
G	93	29.3	70.6	41.3

<sup>1</sup> These values are in accordance with literature [8, 9, 13].

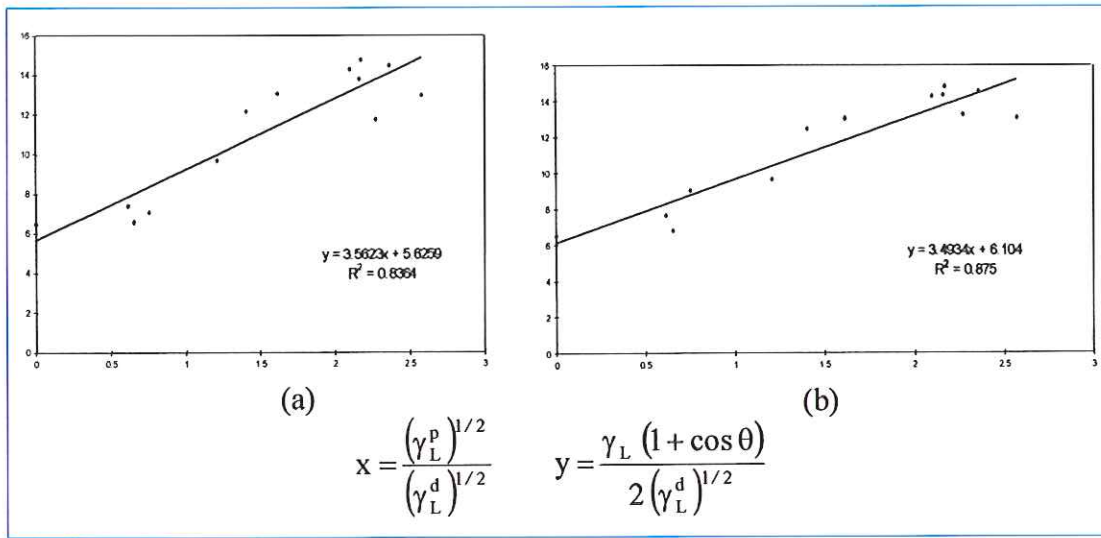


Fig. 6 – Surface free energy evaluation for cement paste (a) and limestone (b).

**Table 5 – Surface free energy of solids**

Support	Surface free energy (mN/m)		
	$\gamma_s^d$ (dispersion)	$\gamma_s^p$ (polar)	$\gamma_s$
Cement + paste	31.65	1.69	44.34
Cement paste + hydrophobic treatment	14.86	0.01	14.87
Limestone	37.08	12.40	49.48
Glass [2]	20.54	22.85	43.39
Silicon paper [2]	12.59	5.41	18

and rock determined by surface topology evaluation. As example, for a surface constituted with 65% limestone and 35% cement mortar, we obtained [2]:

$$\gamma_s^{\text{concrete}} = 0.65\gamma_s^{\text{limestone}} + 0.35\gamma_s^{\text{cement mortar}} = 47.68 \text{ mN/m.}$$

#### 4. DISCUSSIONS

The evaluation of these parameters is fundamental for the study of interface stability; this can be analysed by calculating work of adhesion, interfacial energy or critical surface energy. Defining this critical surface energy ( $\gamma_C$ ), Zisman shows a practical way in order to assess the wettability of solid surface energies (Fig. 7). The idea is that a solid surface will be wetted from liquids with surface energies below the critical surface energy of the solid.

Calculation of  $\gamma_C$  for different supports (Table 6) gives information about the opportunity of wetting the

$$\frac{\gamma_L (1 + \cos \theta)}{2 (\gamma_L^d)^{1/2}} = (\gamma_s^p)^{1/2} \cdot \frac{(\gamma_L^p)^{1/2}}{(\gamma_L^d)^{1/2}} + (\gamma_s^d)^{1/2} \quad (6)$$

This work was realised for the 7 centrifuged slurries, distilled water, reference liquids and the 3 solid supports (Fig. 6).

Table 5 gives the values of solid surface free energy, in comparison with glass and silicon paper [2].

It appears clearly that the dispersion interaction is quite larger than the polar one, especially for cement paste with hydrophobic treatment. It is possible to evaluate  $\gamma_s^{\text{concrete}}$  by application of a ratio between the surface of the concrete really occupied by respectively mortar

**Table 6 – Critical surface energy of solids**

Support	Critical surface energy $\gamma_C$ (mN/m)
Cement paste	25.5
Cement paste + hydrophobic treatment	24.6
Limestone	42.5

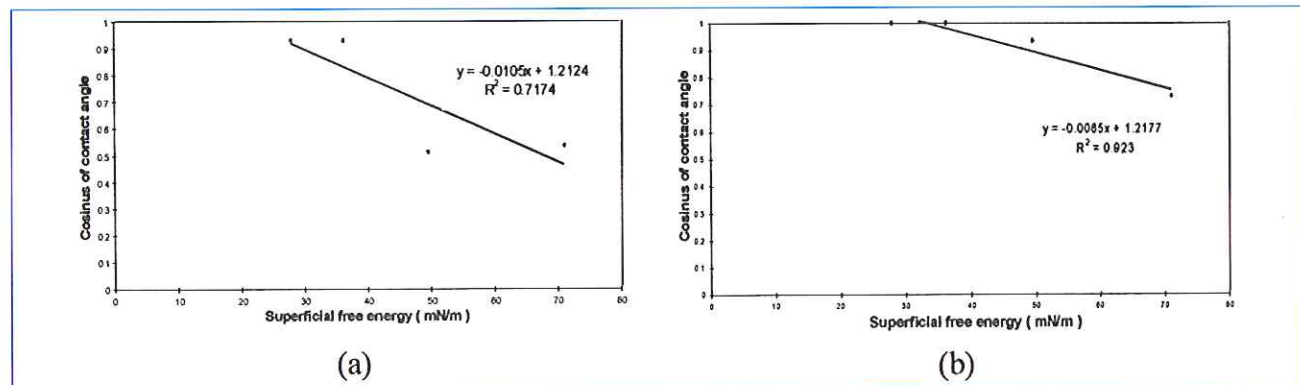


Fig. 7 – Zisman plots for cement paste (a) and limestone (b).

Material	Surface energy (mN/m)
Water	71.1
Cement slurries [2]	70.6
Polystyrene [8]	32.1
Polyvinylacetate [8]	28.6
Polymethylmetacrylate [8]	32.3
Polydimethylsiloxane [8]	14.1
Epoxy resin DGEBA [5]	50
Epoxy resin (triglycidic ether of glycerol) [5]	44.5 - 43
Reactive dilutant (DGEBD) [5]	47 - 45

Liquid	Cement paste	Cement paste + hydrophobic treatment	Limestone	Concrete
A	99.76	101.46	103.49	102.18
B	102.36	104.08	106.14	104.82
C	102.99	104.94	107.15	105.7
D	84.04	85.35	86.98	85.95
E	100.58	102.28	104.31	103
F	98.58	100.18	102.13	100.89
G	106.69	108.81	111.18	109.61
Water	102.49	104.19	106.23	-

mineral surfaces with cement slurries: no centrifuged solutions of cement modified slurries has a surface energy lower than critical surface free energy and, consequently, is able to wet perfectly the concrete surface.

But it appears also easier to wet limestone than cement surface, which could explain particular good adherence between cement mortars and calcareous aggregates.

It is also evident that resinous materials are developing better adherence due to a lower surface free energy (Table 7).

Epoxy resins, polymethylmetacrylate, polyvinylacetate and polydimethylsiloxane for example easily fulfil this criterion.

Moreover, Dann [14] demonstrated that when a liquid series possessing only dispersion forces is used, the critical surface free energy equals the dispersion force component of the surface free energy of the solid and consequently provides a method for determining the true surface free energy of the solid. This way of analysing should be investigated.

The interface stability may be evaluated by the calculation of the work of adhesion that represents the work necessary to separate support and adherent. If adherence is only due to Van der Waals forces, work of adhesion is given by:

$$W_A = \gamma_L + \gamma_S - \gamma_{SL} \quad (7)$$

Taken into account the equation of Owens and Wendt (Equation (2)), evaluation of work of adhesion is given by:

$$W_A = 2(\gamma_L^d \cdot \gamma_S^d)^{1/2} + 2(\gamma_L^p \cdot \gamma_S^p)^{1/2} \quad (8)$$

Different values of polar and dispersive components of liquids and solids previously determined led us to calculate  $W_A$  (Table 8).

Values we have determined here are relative to the relation between slurries (liquid) and concrete support (solid): it does not represent a relation solid/solid and work of adhesion does not evaluate the state and intensity of interaction between hardened products. However, it may give information about the appetency [2] of the

liquid for solid phase and eventual correlation with adhesion properties.

## 5. CONCLUSIONS

The basic measure of wetting is the contact angle that a liquid will make when in contact with a solid adherent. It is really necessary to appreciate and to compare the “appetency” [7] of liquid for solid surface and vice-versa. But if we need to quantify exactly the solidity of the bond, the evaluation of the surface free energy of the bodies to be associated will require sophisticated test devices and measurements. And these are not always well adapted to the particularities of mineral substrates like cement paste and concrete due to problems of roughness, capillary suction and chemical heterogeneity of the surface.

A large area of investigations is open for a better approach of these parameters and a new way for surface free energy measurement of porous solid surface based on capillary suction itself: the speed of absorption is directly in relation with the physico-chemical interaction between liquid and solid and, consequently, with contact angle and surface free energy of liquid.

Another consideration is the influence of water as an interfacial phase between liquid adherent and solid substrate: it modifies values of critical surface energy and work of adhesion and the equilibrium will depend on the respective values of the tension of adhesion. The liquid offering the higher tension of adhesion will expel the other liquid from the surface.

These considerations will be presented in a next article in correspondence with adhesion measurements.

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