

HOW TO ANALYSE THERMODYNAMIC PROPERTIES OF SOLIDS AND LIQUIDS IN RELATION WITH ADHESION ?

Courard L.

University of Liege, Department of Construction Materials, Belgium

Abstract

The theory of adhesion is based on mechanical adhesion, related to macroscopic roughness, and on specific adhesion, explained by means of chemical bonds, thermodynamic approach and intermolecular bonds.

The aim of the paper is an analysis of the contribution of the thermodynamic considerations on the explanation of the adhesion properties developed between a concrete support and a cement slurry.

The measurement of the surface free energies of liquids and solids have been realised by means of Wilhelmy plate method and contact angle measurements. Special surfaces have been prepared to measure the contact angle on cement paste and limestone in order to represent the surface of concrete support. Centrifugated solutions of different cement slurries – modified with admixtures in order to reduce the superficial tension – have been prepared and analysed. Disperse and polar components have been calculated by using reference liquids and solids.

Finally, the work of adhesion and the interfacial tensions were estimated and used, as well as contact angles, as criteria for prediction of adhesion. Some trials of correlation are presented. Large theoretical developments and many bibliographic references will support our measurements and calculations.

1. Introduction

There are few phenomena so diverse as those united under the name of "adhesion". The diversity may involve the nature of two solid bodies and the nature of the medium. Moreover, it is necessary to emphasise a point that is usually ignored : the duality of the term "adhesion" [1].

On the one hand, adhesion is understood to be a process through which two bodies are brought together and attached (bonded) to each other, in such a manner that external force or thermal motion is required to break the bond. The term "adhesion" (or "sticking") is usually applied in this sense in colloid research on coagulation phenomena. As is well known, studies in this area [1] have established that particle sticking generally requires that a certain barrier be overcome by means of external force or thermal energy. On the other hand, we may examine the process of breaking a bond between bodies that are already in contact; and here, as a quantitative measure of the intensity of adhesion, we can take the force or energy required to separate the two bodies.

Adhesion has therefore two different aspects, according to whether our interest is mainly (1) in the conditions and kinetics of joining the bodies or (2) in the separation process.

The intensity of adhesion is influenced not only by the process through which the bodies are brought together, but also by processes at the molecular level in the direct contact zone. Here the process of attachment (bonding, sticking) is of special interest, since the development of this process determines the resistance of the contact to breaking, i.e., the quantitative measure of adhesion.

It is the reason why some authors are promoting the use of the word "bonding" or "sticking" for the processes through which a molecular bond between the two bodies is established and progressively developed with time, and to reserve the term "adhesion" to denote the strength that this bond achieves.

The "bonding" phenomenon may be approached by means of thermodynamic considerations about liquids and solids coming into contact at the interface. The determination of the superficial properties of concrete as well as the one of cement modified slurries, used as impregnation layers for repair systems, is largely described by the author [2]; the aim is here to present the criteria based on thermodynamic properties of materials that will eventually permit to predict adhesion.

2. Wettability of solid surfaces by liquids

The contact between the adhesive and the solid – in our case cement slurry and concrete support – is the result of the wetting procedure [4]. Relation between contact angle and free energies of liquid and solid is described with the equation of Young and Dupre :

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

with γ_{SV} = surface energy of solid/vapour
 γ_{LV} = surface energy of liquid/vapour
 γ_{SL} = interfacial energy solid/liquid

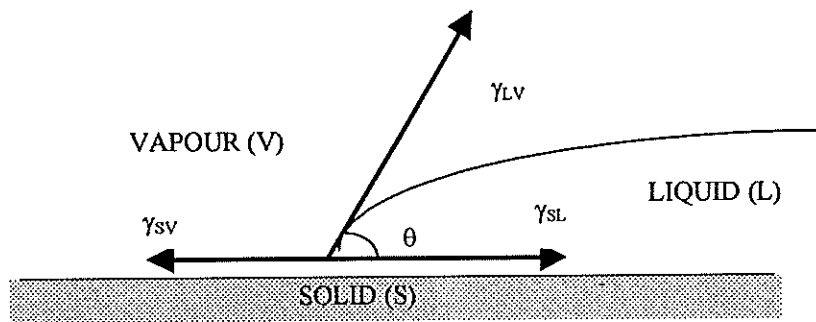


Figure 1: Wetting conditions of a solid by a liquid

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, as well as surface energies of liquid and solid, can be specified in two terms relatively to polar (γ^p) and dispersive (γ^d) interactions. Owens and Wendt [4] gave the definition of γ_{SL} as the geometric mean between these two effects :

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

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 :

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

Surface energy of liquid is evaluated with a tensiometer while contact angles can be determined with a goniometer.

3. Surface energies of liquids and solids

3.1. Surface energy of liquids

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

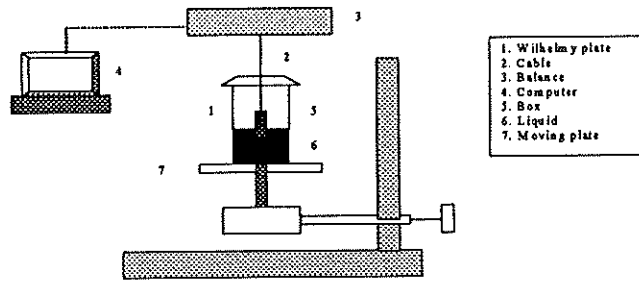


Figure 2: Wilhelmy plate tensiometer

We analysed the centrifugated solution [2] of 8 different cement slurries modified with admixtures used to decrease viscosity (melamine, vinyl copolymer, maleic acid,...). The seventh solution is coming from a pure cement slurry.

Table 1: Surface energies of cement slurries modified or not with admixtures

Mix	Temperature (°C)	Surface energy (mN/m)
I	23.5	66.3
II	23.3	70.3
III	23.2	67.3
IV	23.3	49.1
V	23.2	67.8
VI	23.3	66.3
VII	23.3	70.6
VIII	23.3	42.4
Water	23.2	71.1

Only solutions IV (vinyl copolymer) and VIII (silice fume and superplasticizer) seem to present different behaviours. Mouton [5] observed that the introduction of a reactive diluant into epoxy resin was producing a decrease of viscosity and superficial tension.

3.2. Surface energy of solids

This work is realised by determining the value of contact angle of reference liquids (with wellknown and non variable surface energies) on a goniometer. Due to the heterogeneity of concrete, the measurement was realised separately of the mortar part and the rock part.

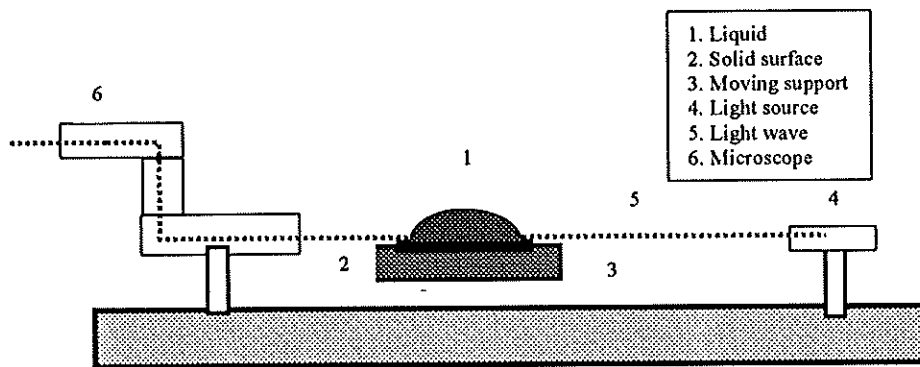


Figure 3: Measurement of surface energy of liquid with goniometer

The same work realised with the 8 different centrifugated solutions of slurries let us to determine, by resolving the equation of Owens and Wendt (equation 3) with linear regression, the values of dispersive and polar components of surface energy of concrete.

In Figure 4, $x = \left(\gamma_L^p\right)^{1/2} / \left(\gamma_L^d\right)^{1/2}$ and $y = \frac{\gamma_L (1 + \cos \theta)}{2 \left(\gamma_L^d\right)^{1/2}}$

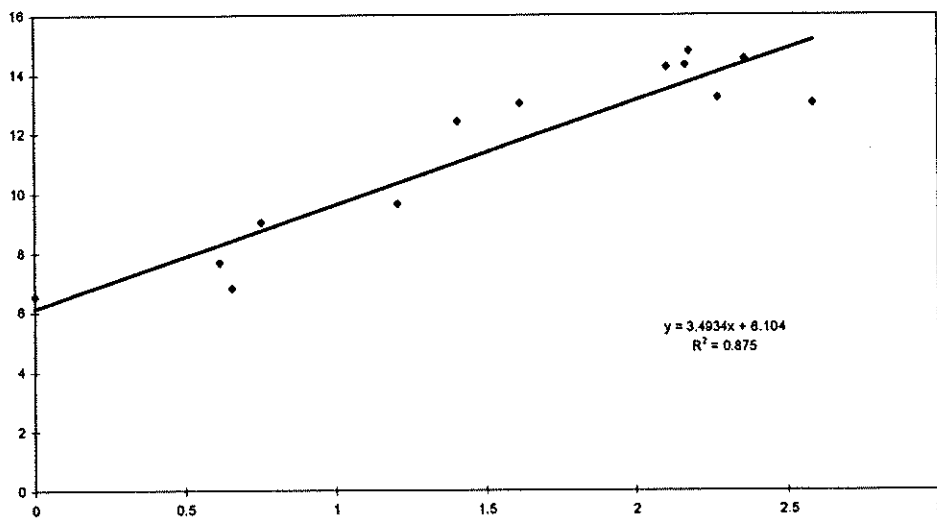


Figure 4: Surface free energy of limestone

Table 2: Evolution of contact angle on a cement paste and limestone rock for centrifugated solutions of cement slurries modified with different admixtures versus time

Liquid	Cement paste		Supports cement paste + hydrophobic treatment		Limestone	
	20 sec.	2 min.	20 sec.	2 min.	20 sec.	2 min.
I	12	9	115	113	16	11
II	17	14	126	123	19	13
III	19	15	130	129	23	17
IV	21	18	122	120	21	16
V	32	29	111	110	23	18
VI	23	21	127	125	29	20
VII	34	31	124	120	21	26
VIII	8	5	103	98	16	8
Water	58	50	120	116	43	35

Table 2 let us to evaluate $\gamma_s^{\text{concrete}}$ by application of a ratio between the surface of the concrete really occupied by respectively mortar and rock (in our case 65 % limestone and 35 % cement mortar).

$$\gamma_s^{\text{concrete}} = 0,65 \gamma_s^{\text{rock}} + 0,35 \gamma_s^{\text{cement mortar}} = 47,68 \text{ mN/m}$$

Table 3: Determination of surface energy of solid γ_s

Support	Surface energy (mN/m)		
	γ_s^d	γ_s^p	γ_s
Cement paste	31.65	12.69	44.34
Cement paste + hydrophobic treatment	14.86	0	14.86
Limestone	37.08	12.4	49.48

4. Analysis of the results

Many criteria are scientifically speaking available to analyse the quality and the stability of the bonding between fresh materials : spreading conditions, work of adhesion or interfacial energy may be used to predict the quality of bonding.

4.1. Spreading criterion

The condition to observe the spreading of the liquid on the solid surface is that the work of adhesion is greater than the work of cohesion of the liquid.

$$W_A > W_C$$

where $W_A = \gamma_L + \gamma_S - \gamma_{SL}$
 $W_C = 2 \gamma_L$

The spreading coefficient may be so defined, incorporating the equation of Young and Dupré (equation 1) :

$$S = W_A - W_C \geq 0 \quad (\text{equation 4})$$

$$= \gamma_L (\cos \theta - 1) \geq 0$$

A negative value for S means a partial wetting of the solid surface and the contact angle θ has a finite value defined by equilibrium conditions. A positive value for S means that the resolution of the inequation is not possible : the spreading is complete and $\theta = 0$.

The criterion clearly represents the fact that the lower the contact angle is, the better the spreading is.

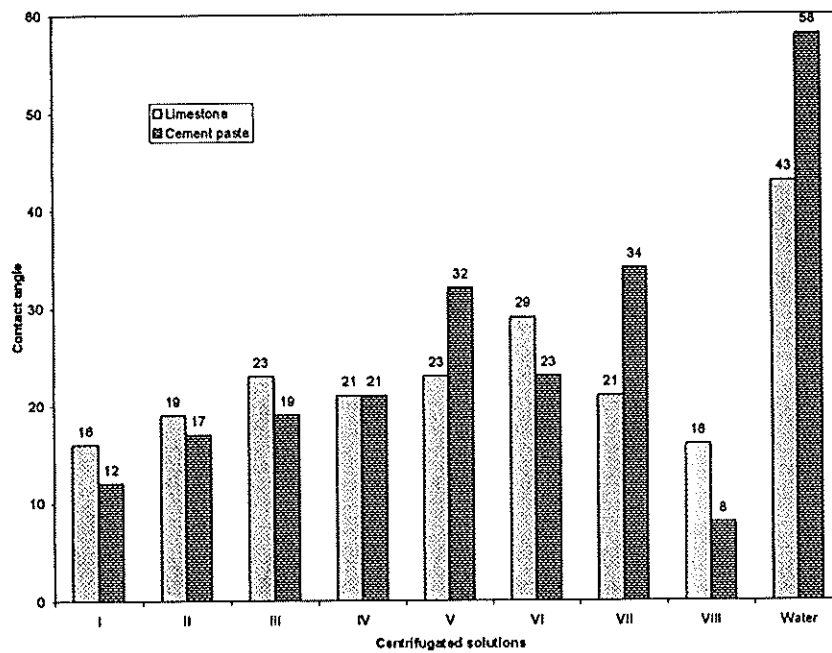


Figure 5: Classification of centrifugated slurries versus contact angle for mortar and limestone

Classification of contact angles for mortar and rock versus the type of slurry let us to have a first choice criterion.

The type of plasticizer or tensio-active admixture plays an important role in the spreading of the slurry.

4.2. Work of adhesion

This notion, already defined herebefore, clearly represents the intensity of the interaction between concrete and slurry : a positive work of adhesion represents a stable interface.

Table 4: Determination of works of adhesion W_A (mJ/m²)

Liquids	Supports			
	Cement paste	Cement paste + hydrophobic treatment	Limestone	Concrete
I	99.76	36.96	103.49	102.18
II	102.36	37.63	106.14	104.82
III	102.99	40.37	107.15	105.7
IV	84.04	29.73	86.98	85.95
V	100.58	37.03	104.31	103
VI	98.58	35.58	102.13	100.89
VII	106.69	43.02	111.18	109.61
VIII	83.62	34.75	87.28	86.01
Water	102.49	37.32	106.23	-

This criterion is however criticable [2] because a high value of W_A means high surface energies of liquid and solid, which is the contrary of good wetting conditions of surface. Hydrophobic treatment hardly decreases values of W_A .

4.3. Interfacial energy

According to the second principle of thermodynamics, the system constituted with the two phases – slurry and concrete – is stable when interfacial energy is minimum.

Gutowski [6] and the author [2] developed this theory, the first one in the case of polymeric materials and the second in the area of concrete repair. The calculation of γ_{SL} may be easily done from the equation of Young and Dupré (equation 1).

Table 5: Determination of interfacial energy γ_{SL} (mN/m)

Liquids	Supports Cement paste	Cement paste + hydrophobic treatment	Limestone	Concrete
I	10.88	44.21	12.29	11.8
II	12.28	47.54	13.63	13.2
III	8.65	41.8	9.62	9.3
IV	9.40	34.24	11.60	10.8
V	11.56	45.64	12.97	12.5
VI	12.06	45.59	13.65	13.1
VII	8.25	42.45	8.90	8.7
VIII	3.12	22.52	4.59	4.1
Water	12.95	48.65	14.35	-

We must remember that this criterion is valuable when the interface is stabilised which means theoretically after hardening of cement or cement modified slurry.

4.4. Critical surface energy

Defining the critical surface energy of wetting of solids (γ_c), Zisman shows another practical way in order to assess the wettability of solid surfaces with different surface energies. The idea is that a solid surface will be wetted from liquids with surface energies which are below the critical surface energy of the solid.

We determined experimentally γ_c for the components of the concrete surface.

Table 6 : critical surface energy γ_c (mN/m)

Support	Critical surface energy (mN/m)
Cement paste	25.5
Limestone	42.5

The results show clearly that no centrifugated solution of slurries present a surface energy lower than the critical surface energy of concrete : that means that none slurry is able to spread completely on the concrete surface.

5. Correlation between thermodynamic parameters and adhesion

This correlation is the way to define "adhesion" as a function of the parameters affecting "binding" or "sticking". The measurement of adhesion was realised by means of pull-off tests of samples made of slurries applied on polished concrete support. As example, figure 6 show the correlation between the work of adhesion and adhesion measured on different samples.

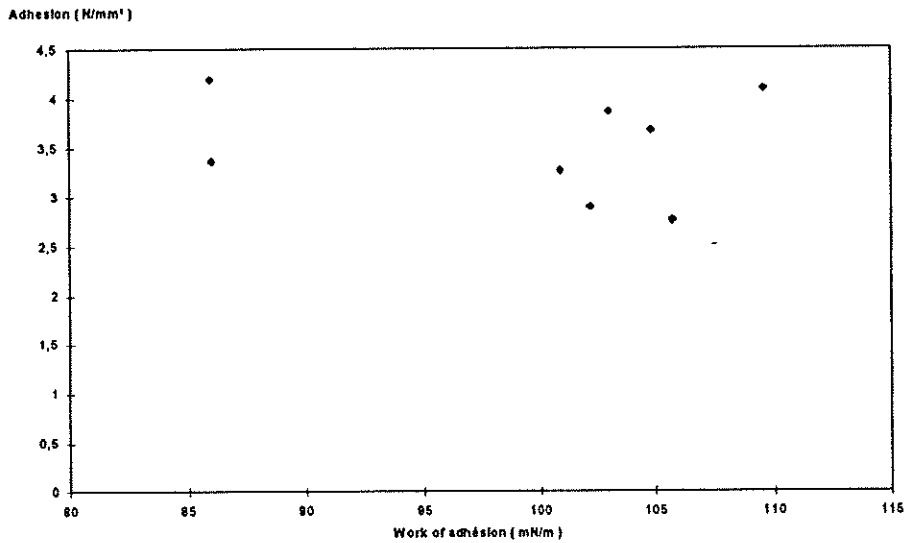


Figure 6: Relation between contact angle and energy of rupture
 In fact, we were not able to find any correlation between the conditions of wetting and adhesion.

6. Conclusions

Many factors affect the relation between thermodynamic properties of liquid and solids, and the measurement of adhesion.

- The test methods used to measure adhesion usually not permit to make distinction between adhesion forces and loss of viscoelastic and plastic energy in the slurry and the concrete support.
- Thermodynamic considerations about stability of the interface may be correlated with adhesion only if rupture happens at the interface. This problem may be partially solved by using characteristic adherence [2].
- Goniometer test method used to measure contact angle on concrete support is not adequately adapted to porous solid. The dispersion on the results is directly related to the difficulties of reading and the heterogeneity of the support.

However, as many other authors [8] [3] [4] [9] [10] [6], I think that contact angle is probably the best way to predict the ability of a slurry or an impregnation layer to wet the concrete surface and consequently, to promote the adhesion. But we must remember that it is only a necessary condition and not a sufficient condition. Many other parameters [7] are influencing the quality and the stability of the interface while rupture mechanics tell us that any crack, defect or heterogeneity at this interface will be the initiation of brittle or instant rupture.

7. References

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