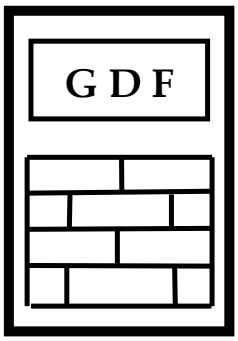
GDF DATA BANKS BULLETIN

High Resolution Mixing Calorimetry
H R M C
Studies of Isothermal Cement Hydration



VOL. 14 , No. 1

Bucharest January 2010

ROMANIA

GDF DATABANKS BULLETIN, VOL.13, NO.3, 2009
ISSN 1453 - 1674

Content

All correspondence at: dragan_gdf@yahoo.com
www.gdfdatabanks.ro

ISSN 1453-1674

This Bulletin is registered at:
- Biblioteca Nationala a Romaniei, Bucharest and
- National Library of Australia, Canberra

GDF DATABANKS BULLETIN, VOL. 14, NO. 1, 2010.
ISSN 1453 - 1674

Studies on cement hydration by high resolution mixing calorimetry.

"Experience – mother of all sciences", Miguel de Cervantes Saavedra

Introduction

High Resolution Mixing Calorimetry (HRMC) [1] has created a new vision on composite structure for a wide category of materials [2], on solubility notion and on the scientific data banks [3]. The basic idea consists in isothermal measurement of thermal effects associated to the mixture of two small test specimens. The high sensitivity, fast response and accurate standard experimental conditions are the main characteristics ensuring high resolution and good repeatability in view to separate elementary processes and to compare samples with subtle structural differences induced by a large variety of treatments. Water and aqueous solutions were the first applications for which further original tests were developed in view to reveal their composite structure in relationship with more and less subtle treatments [4]. For instance these techniques were successfully applied to homoeopathic dilutions [5].
It is important to note that published and here cited references represent a small part of applications and results obtained with these techniques, especially HRMC.
On the other hand, HRMC can be used in non-isothermal conditions by using one specimen [2-5]. Specific heat is another important quantity obtained by HRMC in accurate and rapid conditions. It contains valuable structural information, but unfortunately its significances are neglected in present.
Interaction of water/aqueous solutions-cement was another important application of HRMC technique in view to reveal structural modifications of each component and the overall features of interaction kinetics [6-9]. The main advantage of HRMC technique applied on water/aqueous solutions is that it reveals in highly efficient conditions their transition temperatures [4]. In contrast, adiabatic calorimetry applied for cement hydration process has the main disadvantage in distorting its kinetics giving erroneous information for practical purposes [10]. The aim of the present report is to present some results obtained with a series of water samples originated from the same tap water whose structure was modified by different magnetic treatments and a series of 5 representative industrial cements.

Experimental

The initial HRMC device [1] suffered successive improvements as it is presented in the pictures.
All experiments considered in the present report were performed at room temperature ($23 \pm 1\ ^0C$).

Cement samples were taken from freshly opened industrial bags denoted as E35, E25, aluminous, super-aluminous and BS12. Different series of experiments were performed by using integral cement specimens and size fractions of 30-40 μm obtained by dry sifting.
Water samples are originated from tap water divided, subsequently treated and denoted as: R (untreated), M (constant magnetic field), A and B (oscillating magnetic field).
For all reported quantities at least 5 different experiments were performed in view to reveal their repeatability.

Results

I. Integral cement samples

Figure 1 reproduces HRMC the typical thermogram obtained by mixing experiment as it shown in the cross section of calorimetric cell. The immediate endothermal effect is due by the hydrated crust on cement particles generally present even for fresh cement [6-9]. However, this parasite effect can be easily controlled by keeping the cement samples in dry condition. The exothermal effect revealed in the first 5-15 minutes is the most important process being sensitive to both water and cement morphology and can predict the properties of end products.
Table 1 presents some results on one cement and three water samples. HRMC experiments allow estimating the hydration rate (k). The compressive strength after 96 days (CS96) measured in standard conditions by using the same water-cement systems shows a direct correlation with HRMC data. The volume shrinkage after 24 hours and 3 months shows the decreasing order R > A > B.

Table 1.

water	k (a.u.)	CS96 (daN/cm^2)
R	3.16 ± 0.6	416 ± 15
A	3.53 ± 0.1	480 ± 11
B	3.75 ± 0.1	498 ± 9

All uncertainty values given in this report define the confidence level of 68.3%.

II. Conditioned cement samples.

The 5 cement samples are sifted and conditioned in dry conditions in view to increase the repeatability of HRMC measurements performed on 0.3 ± 0.01 ml water and 200 ± 0.1 mg cement.
Figure 2 shows the integral hydration energy released in the first 5 minutes for all water and cement samples.

Figure 3 presents the same results, but in dimensionless units obtained by reporting the absolute values for activated water samples to the untreated water.

Concluding remarks

a. The main advantages of HRMC technique are: (i) ensures true isothermal conditions in comparison to adiabatic calorimetry taking into account that water/aqueous solutions and hydration kinetics suffer dramatic changes over approx. +40 ^{0}C; (ii) high sensitivity allowing to separate elementary processes; (iii) high repeatability; (iv) it is a rapid analysis allowing the collection of a large experimental data in short time; (v) simple and cheap able to be adopted as a routine test.
b. The early stage of cement hydration is able to reveal structural features both for water/aqueous solutions and cement predicting the properties of the end products.
c. The rate of cement hydration results to be directly correlated with the properties of the end products.

References

[1] G. Dragan, Study of ionic salts-water interactions by high resolution calorimetry. I. Calorimeter and standard measurements, J.Thermal Anal., 31(3), 679-691 (1986); II. General remarks on some sulphates, J.Thermal Anal., 31(4), 941-954 (1986); III. Topoenergetic aspects of dilution process of several sulphates, J.Thermal Anal., 32(1), 293-300 (1987); Some considerations upon coherency in topoenergetic terms. I. High resolution mixing calorimetry (HRMC) experiments on aqueous solutions, J. Thermal Anal., 36 (3), 425-431 (1992).

[2] G. Dragan, High resolution mixing calorimetry (HRMC) in studies of composite systems, Rev. Roumaine Chim., 32(8), 759-765 (1987).

[3] G. Dragan, Solubility behaviour introducing topoenergetic working principles, GDF Databanks Bull., 1(1), 10–18 (1997).

[4] G. Dragan, Comparative study on molecular associations in solid and liquid phases of aqueous solutions. I. Presentation of high resolution mixing calorimetry, DSC, dynamic thermal densimetry and thermo-mechanical analysis, Acta Polymerica, 38(4), 211-220 (1987); II. Topoenergetic representation of behaviour of several sulphates, Acta Polymerica , 38(5), 270-276 (1987); III. Topoenergetic considerations on electric conductivity in electrolyte solutions, Acta Polymerica, 38(8), 467-470 (1987).

[5] G. Dragan, An actual view of physics on homoeopathic practice, Studii si Cercetari de Fizica (Bucharest, Romania, text in English), 43 (7,8), 495-506 (1991).

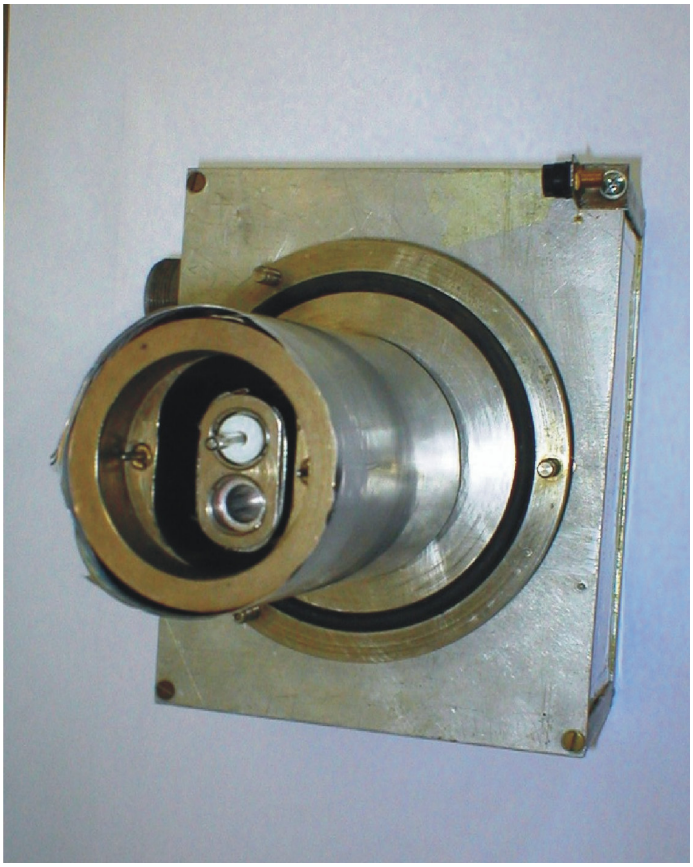
[6] G. Dragan, S.Ifrim, Georgeta Popescu and I. Mindru, Study by HRMC of adsorption of aqueous solutions of super plasticizer additive on cement particles, Rev. Roumaine Chim., 32(8), 767-773 (1987).

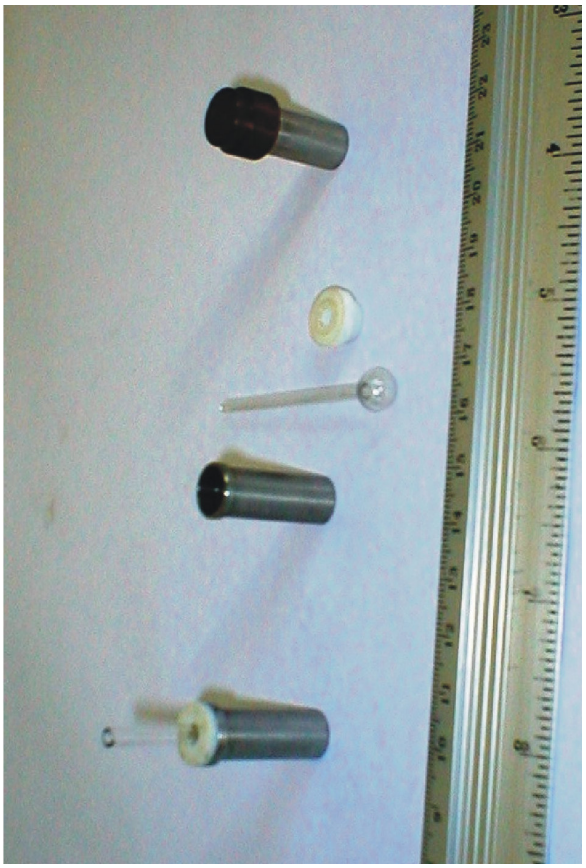
[7] G. Dragan, I.Mindru, Georgeta Popescu and S. Ifrim, Measurements of thermal effects of molecular aggregation of surfactants, Studia Universitaria Babes-Bolyai (Cluj-Napoca, Romania, text in English), 32 (1), 725-729 (1987).

[8] G. Dragan, Georgeta Popescu and S. Ifrim, Thermal effects of micellization of surfactants, Studia Universitaria Babes Bolyai (Cluj-Napoca, Romania, text in English), 32(1), 77-82 (1987).

[9] G. Dragan, Calorimetric study of hydration kinetics of some industrial cements with activated waters, unpublished data, ICECHIM, March 1989; AMCO-SA, January 1991, Bucharest, Romania.

[10] G. Dragan, Adiabatic calorimetry – summary description of the demo prototype, GDF Databanks Bull., 12(3), 2008.





HRMC basic disposition: general view, top view for mixing experiment and details of calorimetric cells (mixing assembly and pressure cell).

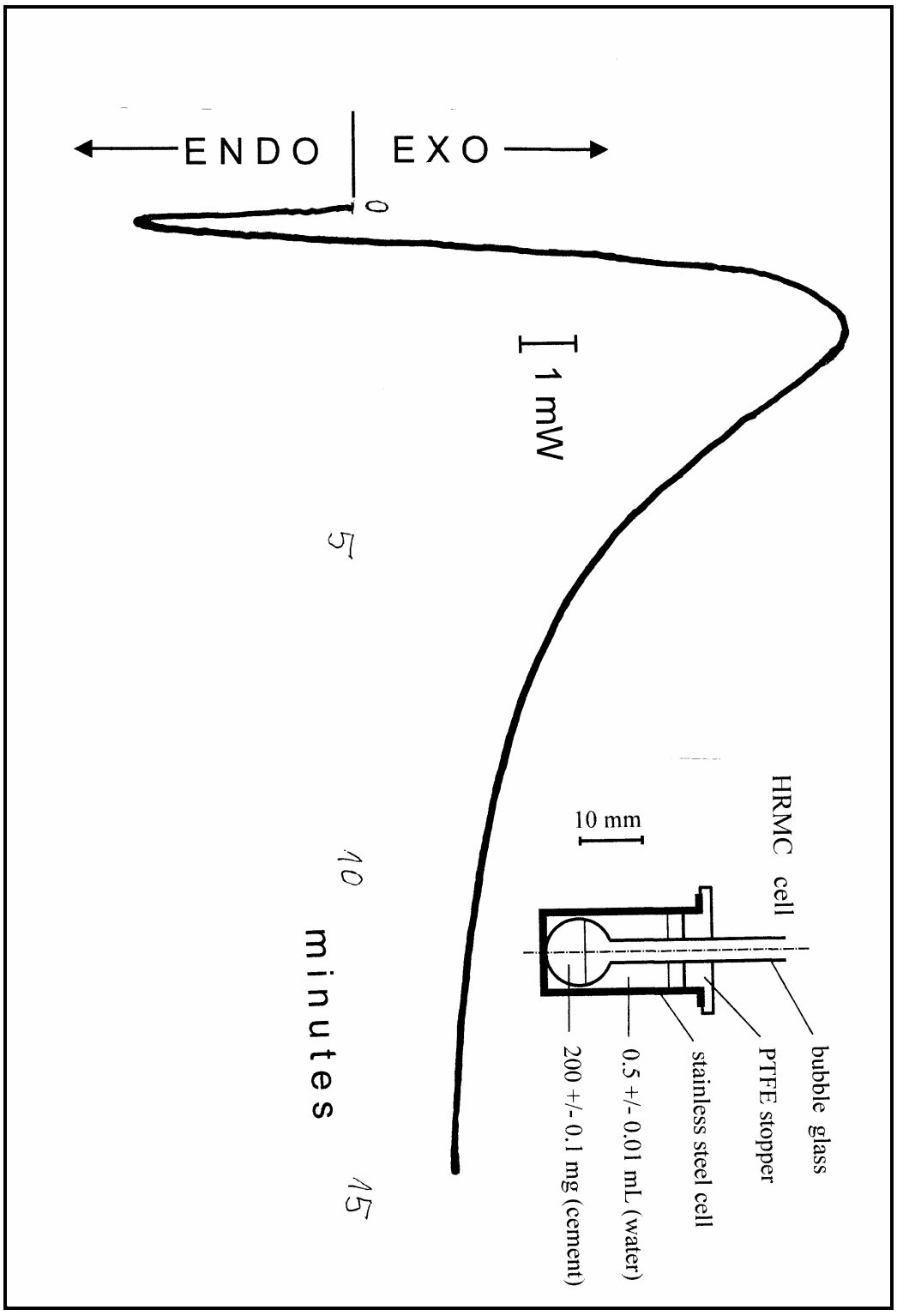


Figure 1. Typical HRMC thermogram of isothermal hydration of cement.

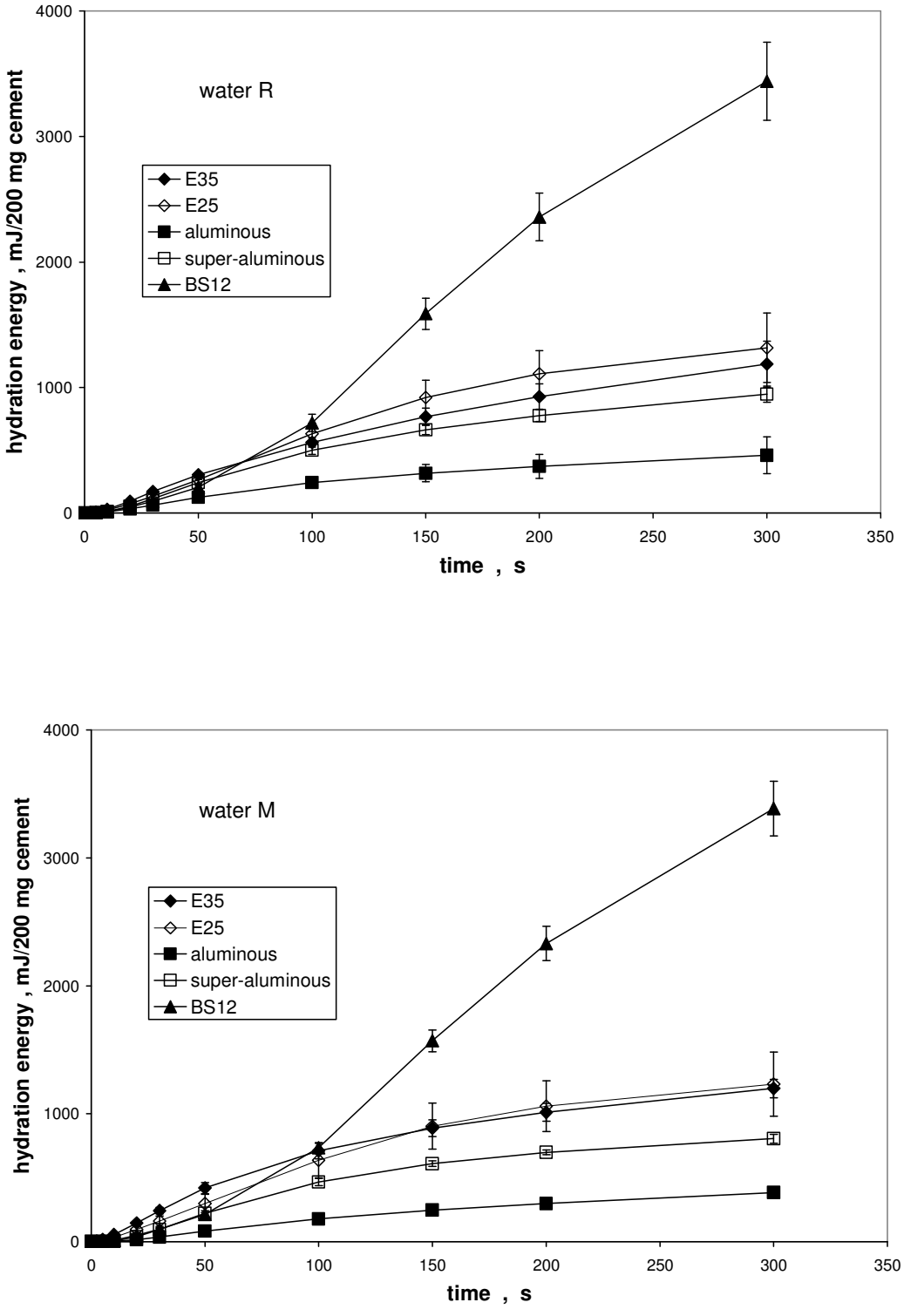
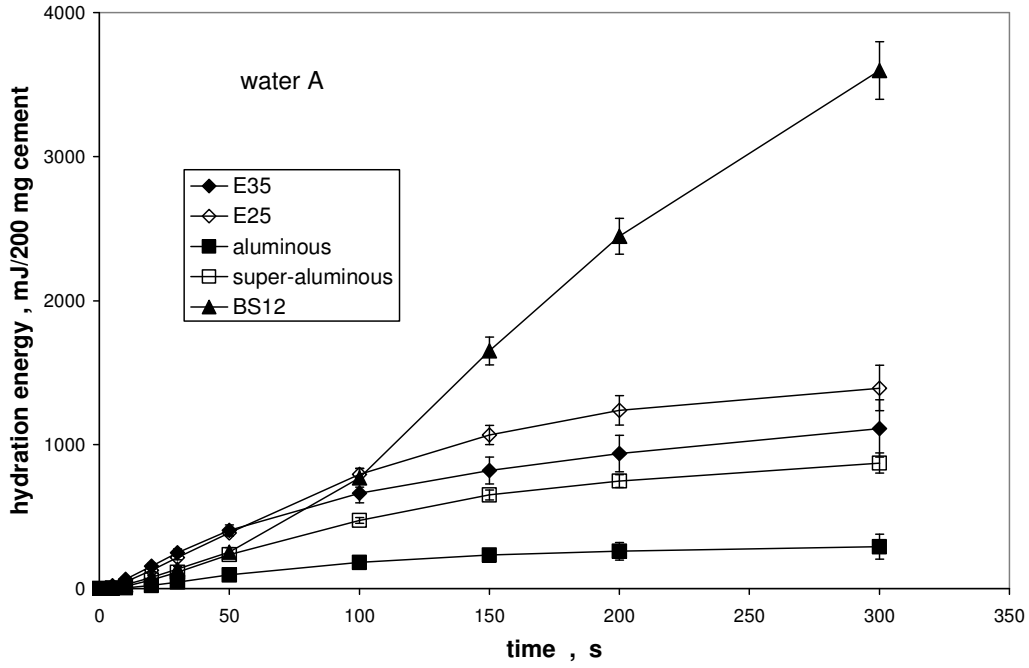


Figure 2. Comparative hydration kinetics for different water-cement systems.



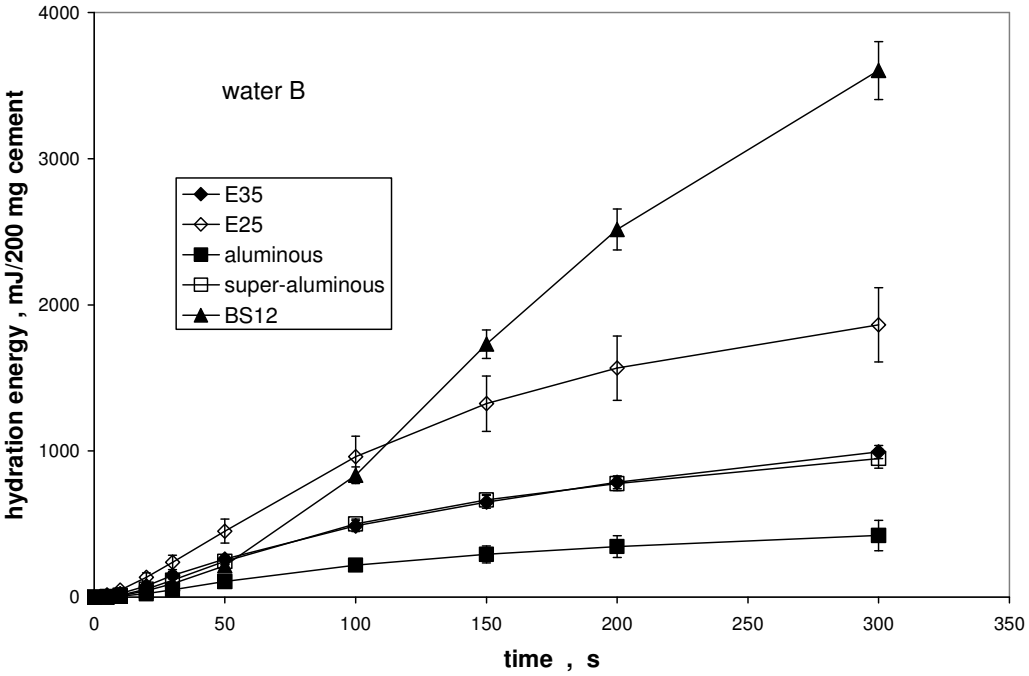
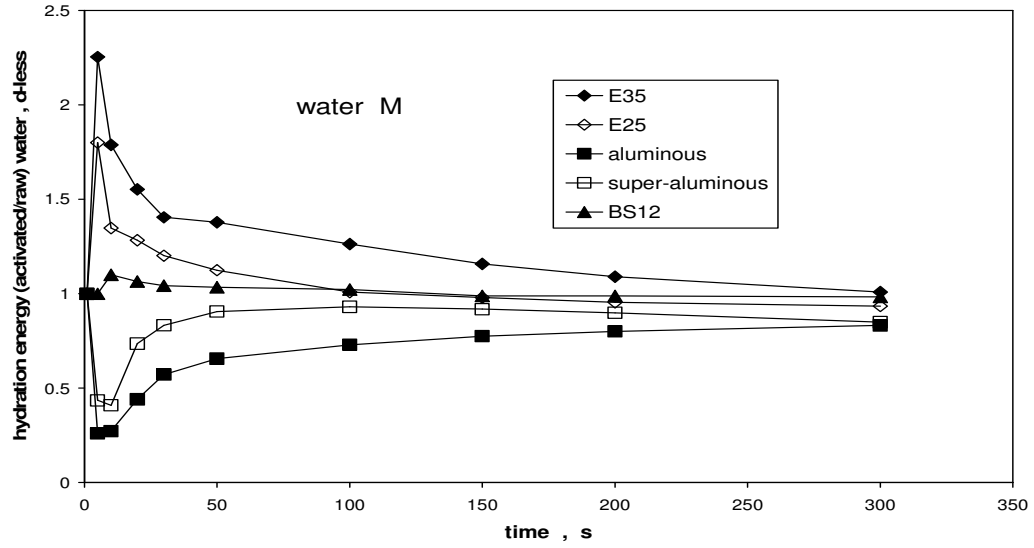
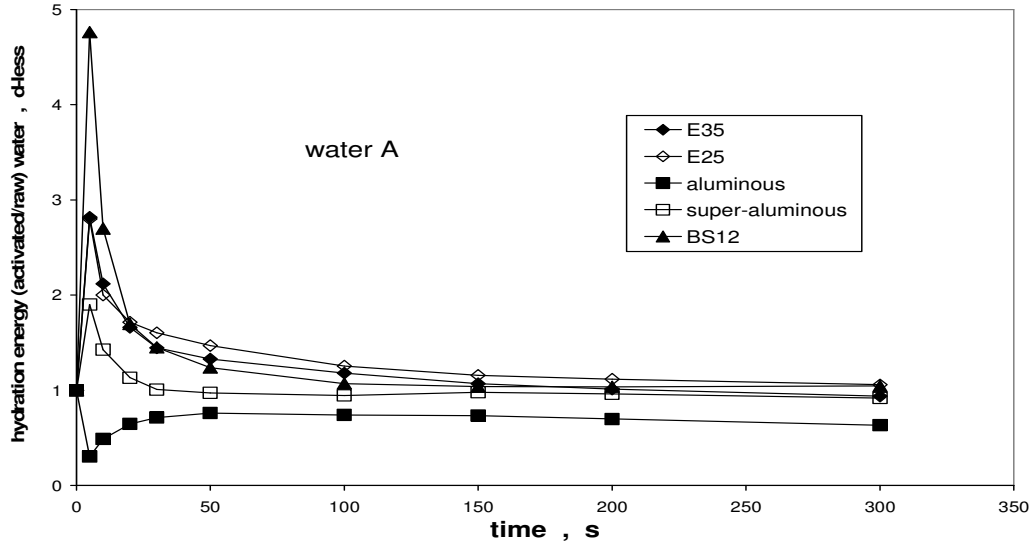


Figure 2. (continued).





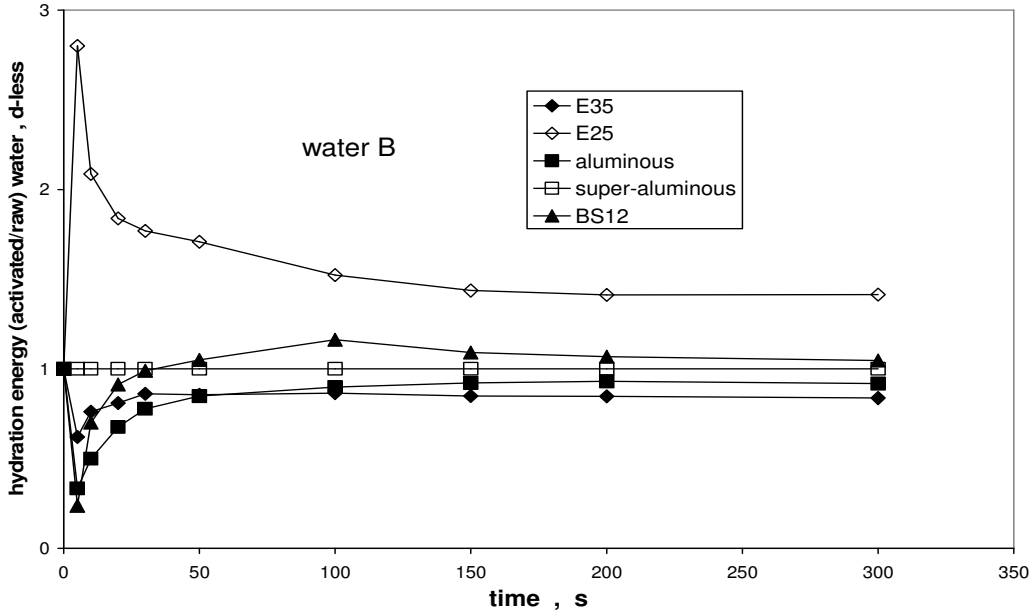


Figure 3. Hydration kinetics of cement samples for each treated water relative to untreated water (R).

ISSN 1453 - 1674

About the author:

First name	Gheorghe
Last name	Dragan
Born	1 September 1945, Ploiesti, Prahova (Romania)
Studies	Faculty of Physics, University of Bucharest, Romania (1963-1968) Ph.D. in Physics, University of Bucharest, Romania (1980)
experience	● Head of material testing laboratory, ICECHIM, Polymer Department, Bucharest (1969-1979); ● Initiator and leader of the research project on new forms and sources of energy; ICECHIM, Center of Physical Chemistry (1979-1988); ● Head of laboratory of analytical devices and measuring instruments, AMCO-SA, Bucharest (1988-1993); ● Technical manager of GDF-DATA BANKS, Bucharest (1993-present); ● Expert metrologist, Romanian Bureau of Legal Metrology, Bucharest, Romania (1997-2000).
publications	● 90 scientific papers ● 70 scientific communications ● 17 patents ● 5 books
Addresses:	Str. Abrud 25, Bucharest 011315, Romania (+40)-(0)21-223-0524, 0733-854-148 c/o 19 Weaver Place Minchinbury, NSW 2770, Australia (0415-674-742, 02-9625-9906) dragan_gdf@yahoo.com

GDF DATABANKS BULLETIN, VOL.14, NO.1, 2010
ISSN 1453 - 1674

Previous issues of GDF DATABANKS BULLETIN

Year	VOL	NO	Content (titles)	$*)
1997	1	1	Editorial: Databanks – the compulsory language. LOGKOW – a Databank of evaluated octanol-water partition coefficients (James Sangster). Solubility behavior introducing topoenergetic working principles. Comments on 1-octanol-water partition of several n-alkane related series.	F
1997	1	2	Guide of good practice in metrology (Romanian)	AFI
1998	2	1	Editorial: socio-psychological implications in creation and utilization of a databank (Ioan-Bradu Iamandescu); Behavior in vapor-liquid equilibria (VLE): I. Structural aspects; Behavior in vapor-liquid equilibria: II. Several structures in databanks; Symposium on VDC-4 held on 30 October 1997 at Lubrifin-SA, Brasov (Romania).	F
1998	2	2	Practical course of metrology (Romanian)	AFI
1998	2	3	DIFFUTOR-01: Thermally driven diffusion in pure metals	AFI
1998	2	4	VAPORSAT-01: Databanks of thermally driven VLE. The first 100 simple molecules	AFI
1999	3	1	Editorial: New trends in material science: nanostructures (Dan Donescu) DIFFUTOR: Databanks of diffusion kinetics. VAPORSAT: Databanks of vapor-liquid separation kinetics.	F
1999	3	2	Discussions on Applied Metrology	AFI
2000	4	1	Editorial: Laboratory accreditation and inter-laboratory comparisons (Virgil Badescu) Doctoral Theses – important data banks. GDF intends to open new series of experiments on thermo-physical properties. Some comments on uncertainty: global budget and DFT analysis. Events: The 9th International Metrology Congress, Bordeaux, France, 18-21 October 1999.	F
2000	4	2	Measurement and Calibration.	AFI
2001	5	1	Editorial: Metrology ensures moral and technological progress. Topoenergetic aspects of amorphous-crystalline coupling. I. Composite behavior of water and aqueous solutions (paper presented at nanotubes and Nanostructures 2001, LNF, Frascati, Rome Italy, 17-27 October 2001). Events: Nanotubes and nanostructures 2000.School and workshop, 24 September – 4 October 2000, Cagliari, Italy.	F
2001	5	2	Editorial: Viscosity – a symptomatic problem of actual metrology. Visco-Dens Calorimeter: general features on density and viscosity measurements. New vision on the calibration of thermometers: ISOCALT® MOSATOR: Topoenergetic databanks on molten salts properties driven by temperature and composition.	F

continued

Year	VOL	NO	Content (titles)	$*)
2002	6	1	MOSATOR-01: Topoenergetic databanks for one component molten salts; thermally driven viscosity and electrical conductance.	AFI
2002	6	2	Editorial: HuPoTest - Operator calibration or temporal scale psychic test. MOSATOR: topoenergetic databanks of one component molten salts; thermally driven viscosity and electrical conductance.	F
2002	6	3	Editorial: Quo vadis Earth experiment? ISOCALT® : Report on metrological tests	F
2003	7	1	Editorial: Time – an instrument of the selfish thinking. 1st NOTE: Homoeopathy: upon some efficient physical tests revealing structural modifications of water and aqueous solutions. I. Mixing experiments.	F
2004	8	1	Metrological verification and calibration of thermometers using thermostats type ISOCALT® 21/70/2. Metrological verification and calibration of thermometers using thermostats type ISOCALT® 2.2R.	F
2004	8	2	Aspects of correct measurements of temperature. I. measurement of a fixed point according to ITS-90. Physics and Homoeopathy: some physical requirements for homoeopathic practice.(Plenary lecture at the 19th SRH National Congress, 21-22 September 2004, Bucharest, Romania)	F
2005	9	1	AWARD for ISOCALT® at the International Fair TIB-2004, October 2004, Bucharest. ISOCALT® 3/70/21 was awarded in a selection of 20 products by a commission of experts from the Polytechnic University of Bucharest. Upon some aspects of temperature measurements. (12th International Metrology Congress, 20-23 June 2005, Lyon, France)	F
2005	9	2	A new technique for temperature measurement and calibration. National Society of Measurements (NSM). Important warning for T-calibrator users: MSA has chose metrology well calibrators from Fluke (Hart Scientific).	F
2005	9	3	Universal representation of Cancer Diseases. 1. First sight on NSW-2003 report. Universal representation of Cancer Diseases. 2. UK cancer registrations on 1999-2002. Vital Potential can estimate our predisposition for cancer diseases.	F
2006	10	1	NTC – thermistors -1	AFI
2007	11	1	HuPoTest - 40 years of continuous research Basic rules for preventing and vanishing cancer diseases Climate change = change of mentality Hot nuclear fusion – a project of actual mentality	F
2007	11	2	MT – Introduction to Mental Technology HuPoTest – general procedure, assignments of results, specimen of complete test , order and obtain your complete HuPoTest report	F

Year	VOL	NO	Content (titles)	$*)
2007	11	3	TRESISTOR© - data banks of materials with thermally driven electric and magnetic properties TRESISTOR© - NTC -1 - data bank of NTC thermistors	AFI
2008	12	1	Australian population: life, death and cancer	F
2008	12	2	Pattern of Cancer Diseases	F
2008	12	3	Adiabatic calorimetry – summary description of the demo prototype	F
2008	12	4	Flight QF 30 and even more… Temperature calibration of NTC-thermistors. 1.Preliminary results.	F
2009	13	1	Proposal for interlaboratory comparisons. Calibration of NTC-thermistors (The 14th International Metrology Congress, Paris, France, 22-25 June 2009)	F
2009	13	2	Sudoku – un algoritm de rezolvare (Sudoku – an algorithm for solution)	AFI
2009	13	3	Cancer and Diabetes – as social diseases (Open letter to all whom it may concern)	F

*) F=free, AFI=ask for invoice.

GDF DATABANKS BULLETIN, VOL. 14, NO.1, 2010
Please feel free to distribute in integral form this issue.
All correspondence at: dragan_gdf@yahoo.com

www.gdfdatabanks.ro

ISSN 1453-1674