

# EVOLUȚIA ÎN TIMP A REACȚIEI ALCALII-AGREGAT PRIN ADITIE DE NANOSILICE COLOIDALĂ EVOLUTION IN TIME OF ALKALI-AGGREGATE REACTION BY ADDITION OF COLLOIDAL NANO-SILICA

Y.A. SORVACHEVA<sup>1\*</sup>, T.M. PETROVA, A.V. POLETAEV, E.Y. CHISTIYAKOV

Petersburg State Transport University, Moskovskiy pr. 9, St. Petersburg, 190031, Russia

*Accelerated tests were conducted to evaluate the potential reactivity of one of the potentially dangerous aggregates from the point of view of combination with high alkaline cement with the measurement of linear expansion deformations in order to study the impact of nano-silica on the process of alkaline corrosion of the concrete and formation of cement matrix. It was revealed by using electron microscopy that the addition of nano-silica in concrete mixture promotes the formation of alkali-silica gel in the cement matrix, but not in the pores of the sample, which contributes to slowing, but not prevention of an alkaline corrosion of concrete.*

**Keywords:** Alkali-aggregate reaction, nano-silica, reactivity aggregates, durability

## 1. Introduction

American scientist T. Stanton established a base of numerous studies in the field of internal corrosion of the concrete in 1940 by publishing information about the destruction of a number of structures which were built between the late 1920s to the beginning of the 1940s in California (Virginia) and called this phenomenon as an alkali-silica reaction (ASR) [1].

Elevated temperature of environment is one of the factors which contributing to this reaction and that's why it was suggested that this problem should not arise in some countries, such as Denmark, northern Germany and the UK, in connection with their geographical location and geological situation. Reports that were published later about damages of some constructions show that it was erroneously.

The destruction of the bridge in Luebeck in 1964 is the first diagnosed case of alkali-silica reaction in northern Germany. Also destructions were observed in such countries as Denmark (1950), Iceland (1960-1970), England (1971), Turkey (1975), Australia (1980), Sweden and Norway (1980-1990), Switzerland (1995), The Netherlands (1995-1998) and Finland (2011). Buildings, bridges, highways, airfield pavements, dams, waterworks and reinforced concrete under-rail structures have been exposed to destructions [2 - 11]. According to the analysis of officially recorded cases of damages of structures due to the

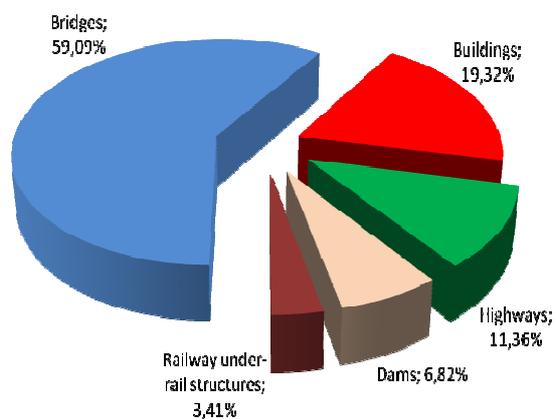


Fig. 1 – Distribution of damages by the type of structures.

AAR worldwide, their classification is shown in Figure 1.

There is almost no statistical data about the destructions of reinforced concrete structures due to internal corrosion of the concrete in Russian Federation, however, reinforced concrete sleepers that have been subjected to alkali-silica reaction after 3 years of exploitation were investigated by authors in 2004 [12].

An application of the active mineral additives such as silica fume, fly ash and ground granulated blast furnace slag is an effective way which used in practice to prevent an alkali-silica reaction, though many aspects are related with their inhibitory effect remain to be elucidated [13,14]. On the other hand, there are some works which show that certain their species may conversely increase the undesirable

\* Autor corespondent/Corresponding author,  
E-mail: ksmit\_pgups@mail.ru

expansion of samples [15, 16].

Currently, there is no specific method for assessment of the impact of active mineral additives on the process of internal corrosion of concrete, there is no information about the required dosage and the size of their particles, and therefore the study was conducted to evaluate the influence of nano-silica on the process of expansion of the samples.

## 2. Materials and methods

### 2.1. Characteristics of materials

It is a well known fact that the maximum allowable content of the alkalis in the cement as 0.6% in recalculation on sodium oxide equivalent was defined in a number of national and international standards.

In this study was purposely used a highly alkaline Portland cement (PC) to provoke an alkali-silica reaction with the following chemical and mineralogical composition (Table 1).

It was gotten that the cement contents 1.19 % of alkalis in recalculation on  $\text{Na}_2\text{O}_{\text{eq}}$  as a  $\text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$  which is in two times higher than the allowable limit.

The crushed coarse aggregate from one of the occurrences in southern Russia was used in the preparation of the concrete samples. It composed of ~ 20-25% of quartz, feldspars ~ 20-25%, 18-20% chalcedony ~, ~ 13-15% amphibole, ore minerals ~ 13-14% pyroxene ~ 3-4% , mica and hydromica ~ 3-4% and 1-2%  $\text{CaCO}_3$  according to the results of petrography analysis.

According to the chemical analysis results it was revealed that the aggregate contains 38.1 mmol/L of amorphous silica, which is on 24% below the limit in 50 mmol/L.

The most reactive minerals of the rocks are opal, chalcedony and quartz with a damaged crystalline lattice which also called amorphous silica. The presence of the last in the used aggregate was validated by the pictures which were made with a polarizing microscope (Fig. 2).

Quartz has a crystalline structure and when the angle of incidence of light is changed one can see an alteration of coloring of the mineral from dark to the light immediately.

It becomes the most active and exposed to influence of alkalis of the cement and called as amorphous silica, when its crystal lattice is disturbed.



Fig. 2 – Quartz with damaged crystalline lattice, x50

In order to prevent the occurrence of the alkali-silica reaction and to reduce the expansion deformations colloidal nano-silica (NS), containing of  $\text{SiO}_2$  - 99.2% with a specific surface area of 300  $\text{m}^2/\text{g}$  in an amount of 0.025 % and 0.125% by weight of cement has been introduced in concrete mixture.

### 2.2. Test methods

Currently, there are two test methods for assessing of the potential reactivity of aggregates: accelerated test (for two weeks) and long test (for 1 year).

The most common technique is presented in American standards ASTM C 1260 and ASTM C 227, the analog of which is national standard of Russian Federation - GOST 8269.0-97.

According to these documents, accelerated tests conducted on samples of size 25x25x254 mm, made of fine-grained concrete mix with ratio of cement and crushed aggregate 1:2.25 by weight. Water-cement ratio is established with a standard method of pre-selection. The samples should be placed in a container with distilled water and incubated for a day at 80 °C after 24 hours of curing in the molds; further, the samples should be stored in a solution of 1M NaOH at the same temperature. Measurements are made daily for two weeks. If the extension of the samples after 11 cycles exceeds 0.1 %, the aggregate is considered as a potentially reactive.

Table 1

Chemical and mineralogical composition of the cement	
Mineralogical composition, %	Chemical composition, %
$\text{C}_3\text{S}$ ( $3\text{CaO}\cdot\text{SiO}_2$ )	52.9
$\text{C}_2\text{S}$ ( $2\text{CaO}\cdot\text{SiO}_2$ )	19.4
$\text{C}_3\text{A}$ ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ )	6
$\text{C}_4\text{AF}$ ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ )	12.5
	$\text{SO}_3$ 2.89
	$\text{SiO}_2$ 20.7
	$\text{Al}_2\text{O}_3$ 5.21
	$\text{Fe}_2\text{O}_3$ 4.15
	CaO / free CaO 63.9 / 0
	MgO 1.75
	$\text{K}_2\text{O}$ 0.60
	$\text{Na}_2\text{O}$ 0.80

In Germany, for example, accelerated tests are carried out on samples of size 40x40x160 mm, made of fine-grained concrete with water-cement ratio of 0.5 with the content of 450 g of the cement and 1350 g of the aggregate which was divided in equal proportions: per 450 g of fractions 0.5-1 mm and 2.1 mm and 450 g of natural nonreactive sand. The samples are kept above the water at a temperature of 70°C for 28 days; the limit of expansion is 0.15%.

The same size samples are used in Denmark, but one should prepare a mixture 1:2 with water-cement ratio of 0.5. After 24 hours of curing in molds, the samples are stored in water, and then are immersed in a saturated NaCl solution at 50 °C. Measurements should be made weekly for 28 days.

**3. Results**

**3.1. Physical and mechanical properties**

A plastic strength of the cement paste has been evaluated at the different time using a conical rheometer to study a structure formation of the cement stone. The effect of colloidal nano-silica on the kinetics of increasing of plastic strength was analyzed (Fig. 3).

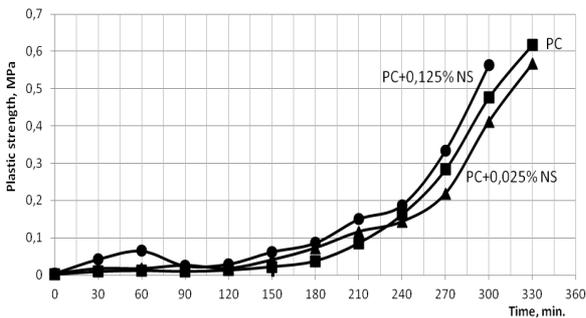


Fig. 3 – Effect of nano-silica on the kinetics of increasing of plastic strength of the cement paste.

Analysis of the graph showed that the addition of colloidal nano-silica has a negligible impact on the setting time of cement paste: it reduces the time of the final setting by increasing the amount of the filler (from 5 h 30 min to 5 hour 00 min), while maintaining the same initial setting time (2 h 30 min).

The presented diagram shows that the period of formation of coagulation structure (induction period of hardening of the cement paste) is not increasing by the addition of the nano-silica. However, by increasing the amount of this filler the time of its transition to coagulation-crystallization structure is decreasing slightly.

To determine the effect of nano-silica on the process of the hydration of Portland cement was carried out a qualitative and quantitative analyzes of samples of cement stone by the standard method with the introduction of 20% of zinc oxide crystalline structure, whereby it was made disregard of the formed peaks of zincite in qualitative analysis (Fig. 4).

Results of the analysis suggest the virtual absence of ettringite in submitted samples (value ranges from 0.97 to 0.46%), due to the small amount of gypsum contents in cement and eliminates the expansion of samples due to its increase in volume. In turn, the introduction of nano-silica accelerates the hydration process and increases of portlandite content on 55%.

**3.2. Expansion of samples due to alkali-silica reaction**

To conduct of accelerated test for the assessment of the potential reactivity of aggregate were made three concrete mixtures with the same water-cement ratio 0.42. Average values of the relative expansion deformations are shown in Figure 5.

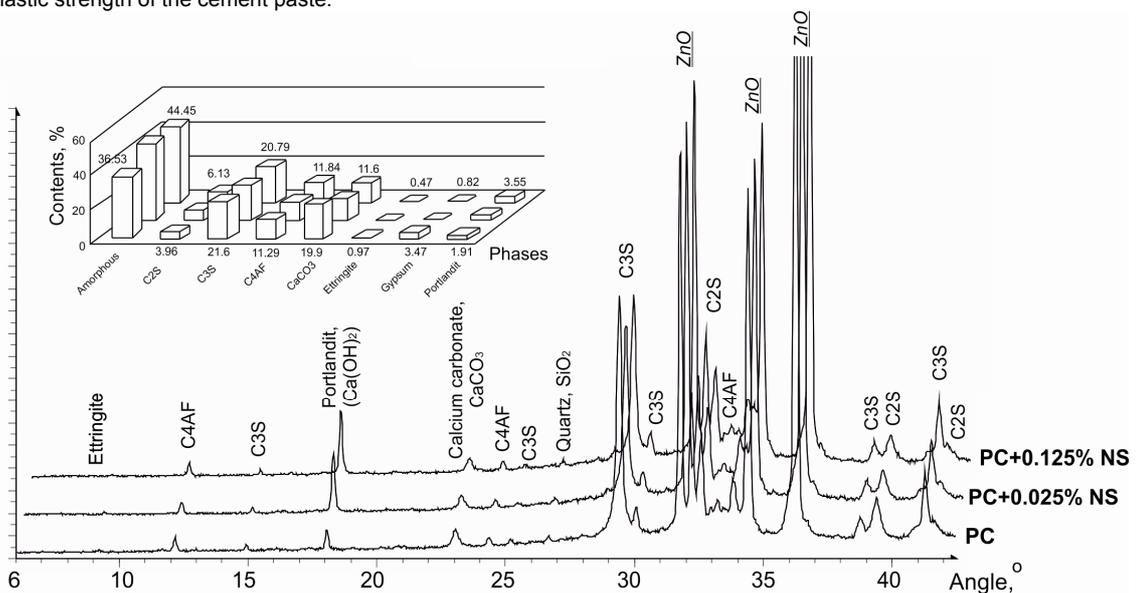


Fig. 4 - Radiographs of samples

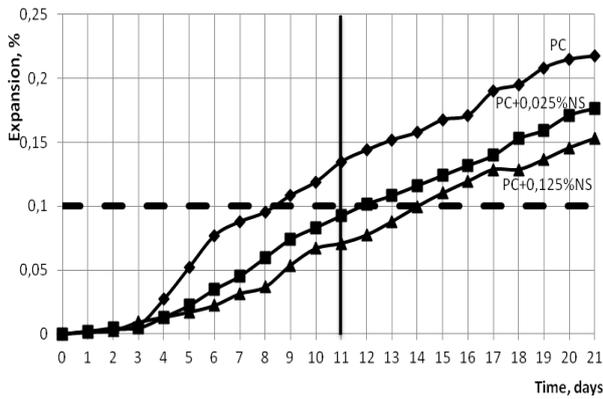


Fig. 5 – The results of the relative expansions of fine-grained concrete samples.

Relative ASR expansion of the control samples reached the value of 0.13 % after 11 cycles of the test, however, deformations of samples with nano-silica in an amount of 0.025 % and 0.125 % by mass - 0.09 % and 0.07 %, respectively.

Based on this results could be erroneously conclude that nano-silica prevents the occurrence ASR. Nevertheless, deformations of the samples and ASR expansion are continuing to increase in NaOH solution after 11 cycles and in 21 day will exceeded the allowable limit in 1.5 - 2 times. The results demonstrate that the addition of colloidal nano - silica does not prevent of ASR, but rather slows it down.

In order to confirm this assumption and to detect the gel in the samples, as a product of alkali-silica reaction, microscopic examination of samples were carried out by polarizing and 3D microscopes (Fig. 6, 7).

It was established that nearly all the pores in the sample without additives are completely or partially filled of alkali- silicate gel, that indicating of ongoing internal corrosion in concrete. The presence of gel in the pores accelerates the expansion of the samples followed by the formation of micro cracks.

In turn, the samples with the nano - silica are characterized by the formation of alkali-silica gel not in the pores, as in the cement matrix, which explains the slowing down of the chemical reaction between the alkalis of the cement and silica of aggregate, and as a consequence, slows expansion manifestations of samples. Figure 8 presents a sample of concrete with 0,125 % of nano-silica.

Alkali corrosion in the cement matrix was confirmed during X-ray microanalysis at EDX2 (Fig. 8). Elemental composition of the gel is shown in Figure 9.

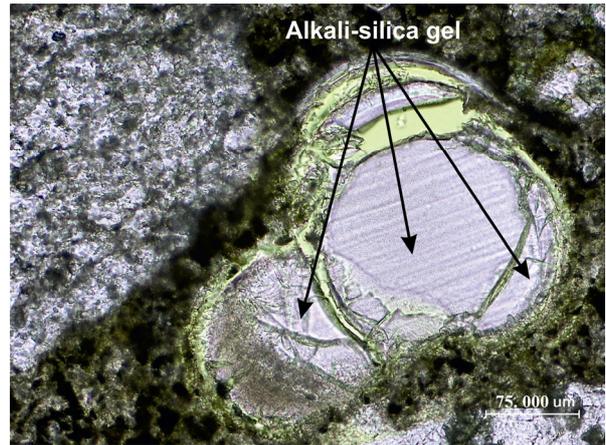


Fig. 6 - The pore is almost filled by alkali-silica gel, x75.



Fig. 7- Pores completely filled by alkali-silica gel near the reactive quartz, x50.

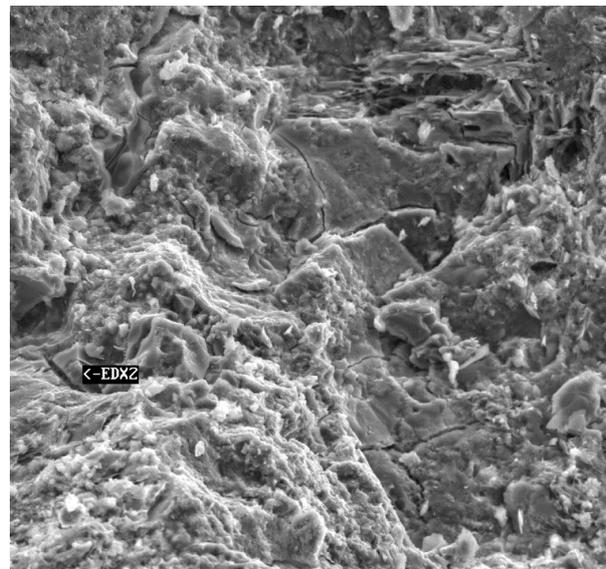


Fig. 8 – Alkali-silica gel in cement matrix, x500

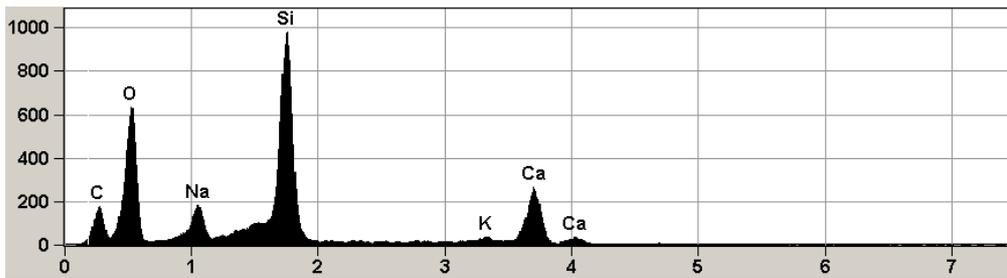


Fig. 9 – The composition of the alkali-silica gel.

From the point of view of quantitative composition, in the illustrated part of gel predominates silica oxid, approximately 64%, sodium oxide in an amount of 9% potassium oxide - 4%, calcium carbonate - 23%.

#### 4. Discussion

An assessment of the factors affecting on the possibility of alkali-silica reaction is one of the necessary conditions for high durability of concrete structures. The compatibility of materials for the manufacture of reinforced concrete structures should be assessed in terms of potential reactivity of coarse and fine aggregates with alkalis of the cement in order to prevent the devastating effects of internal corrosion of the concrete.

In case of receive unwanted expansions of the concrete in laboratory conditions it is necessary to develop measures of prevention of the occurrence of internal corrosion, either to replace the aggregate or to use an active mineral additives.

Holding of the accelerated tests is not enough to obtain an objective assessment about the potential reactivity of aggregates and it is necessary to make additional microscopic studies to detect an alkali-silica gel in the structure of the concrete or to use a long test method.

#### 5. Conclusions

The combination of the cement with 1.19% of alkalis in recalculation in  $\text{Na}_2\text{O}_{\text{eq}}$  and crashed coarse aggregate containing 38.1 mmol/L of amorphous silica was used in this study. The relative expansion of the concrete samples achieved the value of 0.13% after 11 research cycles and that exceeds the limit of accelerated test method on 30 %.

Colloidal nano-silica in amount of 0.025% and 0.125% by cement mass was added in the concrete mixture to prevent of ASR and after 11 cycles relative expansions had been decreased till 0.09% and 0.07% respectively.

Nevertheless, deformations of the samples and ASR expansion are continuing to increase in NaOH solution after 11 cycles and in 21 day will exceeded the allowable limit in 1.5 - 2 times.

The results obtained in the study suggest that the use of nano-silica allows only slow down of

alkali-silica reaction and not prevent it. Slowing of reaction due to the formation of the gel is not in the pores as in the cement matrix, in connection with which, in the latter case, requires a much greater amount of gel which could lead to an undesirable expansion of the samples.

It is not always possible to make a correct conclusion about the effect of the active mineral additives on the ASR according to the accelerated test method what can be explained by their low duration and aggressive environment of this test.

#### Acknowledgements

*This work has been financed by the Scholarship of the President of Russian Federation for studying abroad and has been made both in Petersburg State Transport University (Russia) and F.A. Finger - Institute of Building materials in Weimar (Germany).*

#### REFERENCES

1. T.E Stanton, Expansion of concrete through reaction between cement and aggregate, Proceedings American Society of Civil Engineers, 1940, pp. 1781-1811.
2. D.W. Hobbs, Alkali-silica reaction in concrete, Thomas Telford Ltd, London, 1988.
3. V. Jensen, Alkali aggregate reaction in Southern Norway, Doctor Technical Thesis, University of Trondheim, 1993.
4. V. Jensen, C. Merz, Alkali-aggregate reaction in Norway and Switzerland – survey investigations and structural damage. In: Broekmans, M.A.T.M. and Wigum, B.J. (eds.) in Proceedings of the 13th ICAAR, Trondheim, Norway, 2008, 785.
5. W. Bodeker, Alkalireaktion im Bauwerksbeton – Ein Erfahrungsbericht. Deutscher Ausschuss für Stahlbeton (DAfStb), Heft 539, Berlin, 2003.
6. J.D. Bakker, ASR in 20 bridges in and over motorway 59 in the Netherlands, in Proceedings of the 8th International Conference on Structural Faults and Repair, London. United Kingdom, cd-rom, 1999, 8.
7. Özge Andiç-Çakır, Oğuzhan Çopuroğlu, and Tetsuya Katayama, A review of alkali-silica reactivity in Turkey: a case study from Izmir, west Anatolia, in Proceedings of the 14th ICAAR, Austin, Texas, USA, 2012, 10 pp.
8. P. Nerenst, Alment om Alkali Reaktionen i Beton (with an English summary). The Danish National Institute of Building Research and the Academy of Technical Sciences, Committee on Alkali Reactions in Concrete, Progress Report AI, Copenhagen, 1957.
9. G. Gudmundsson and H. Asgeirsson, Some Investigation on Alkali Aggregate Reaction, 1957.
10. Lagerblad & Trägårdh. Alkali-silica reactions in Swedish Concrete. Stockholm (in Swedish), 1992.
11. H. Pyy, M. Ferreira, E. Holt, Assessing the extent of AAR in Finland. In: Drimalas, T., Ideker, J.H. and Fournier, B. (eds.), in Proceedings of the 14th ICAAR, Austin, Texas, USA, 2012, 6.

12. T.M. Petrova, Y.A. Sorvacheva, To the question of the durability of the reinforced concrete structures, Modern directions of theoretical and applied researches, 2013, **43**(1), 68.
13. J. Lindgard, Alkali-silica reactions (ASR): Literature review on parameters influencing laboratory performance testing, Cem. Concr. Res., 2012, **42**(2), 223.
14. A.S. Brykov, M.E. Voronkov, M.V. Mokeev, Inhibitory activity and transformation of mineral additives in testing of cement compositions for alkali expansion, Cement and its Applications, 2012, **6**, 111.
15. S. Diamond, Alkali-aggregate reactions in concrete – Pore solution effects. In: Idorn, GM, and Rostam, S (editors), in Proceedings of 6th International Conference on AAR in Concrete, Copenhagen, Denmark, 1983, 155.
16. J. Duchesne and MA Bérubé, Effectiveness of supplementary cementing materials in suppressing expansion due to ASR: Part 2 Effect on the pore solution chemistry, Cement & Concrete Research, 1994 (24), 221.

\*\*\*\*\*

## MANIFESTARI ȘTIINȚIFICE / SCIENTIFIC EVENTS



EMR2015 will bring together researchers and professionals from a broad set of science and engineering disciplines with the aim of sharing on the latest developments and advances in materials and processes involved in the energy generation, transmission-distribution and storage. The connection is clear between research into novel materials and new technological solutions or improvements in materials, and the development of cleaner, cheaper safer and more efficient energy technologies.

This conference will provide an excellent opportunity for everyone involved to learn and discuss about materials, processes and systems applied to the following areas:

- Energy production from Biomass - Biofuels
- Nuclear Energy and Materials
- Solar Energy
- Energy Production from Fossil Fuels
- Energy Harvesting Materials
- Fuel Cells
- Energy Transmission, Distribution and Storage
- Hydrogen
- Advances in Lighting Materials
- Wind Power
- Energy-Efficient Buildings
- Geothermal Energy
- Materials, Processes and Systems for Energy Saving and Sustainability
- Hydropower. Wave and Tidal Power

**Contact:** <http://www.emr2015.org>

\*\*\*\*\*