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A CASE STUDY OF ALKALI-SILICA REACTION IN HIGH-DENSITY CONCRETE

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ABSTRACT

In 1991, after three years of use of a γ-ray machine located in an hospital devoted to cancer treatment, a study was carried out in our laboratory to explain the surface degradation of high-density concrete used in massive walls and ceiling as radiation protection. Surface problems, appeared during the first year of use of the machine, consisting in pop-outs, exsudations of gel, and very localised cracks. Since 1994, annual periodical measurements have been carried out (surface defaults, relative deformations, crack opening, and composition of gel).

Macroscopic observations show systemically a bloody red aggregate at the bottom of crater and a gel flow on the edge. Microscopic observations (polarised light) reveal that blood-red aggregate is mainly composed of hematite associated with goethite, limonite, and micro quartz. As the association between the bloody red aggregate and the pop-outs is established, it seems that the expansive transformation of goethite to limonite is the main cause of expansion, the rate of transformation being accelerated by the γ-ray environment.

Chemical analysis of internal gel shows an unusual composition when compared to the literature since it only includes silica and a high level of potassium or sodium ions. This alkaline silica gel, which exists in the concrete without microcracks seems to be not expansive. More, ettringite and gel enriching in calcium, missing during the first observations or analysis, have appeared later and are affected by some cracks. In this case also, the γ-ray exposure seems be responsible for the rate of reaction.

In conclusion, it seems that radiation can initiate and accelerate an alkali-silica reaction in concrete cast with reactive aggregate. So a question may be asked : "will alkali-silica reaction occur in containers of stored nuclear waste ? "

Keywords : Alkali-silica reaction, hematite, high-density concrete, γ-rays.

INTRODUCTION

In 1991, a study was begun to our laboratory in order to explain the origin of surface degradations appearing on high-density concrete in a hospital. This high-density concrete is used to protect the personnel from γ-rays emitted by the particle accelerator used for cancer treatment. Problems of surface degradation, appeared in the first year of machine use, consisting of the appearance of craters and swellings as well as cracks.

We present the analysis of phenomena observed in 1991, after three years of use of the accelerator, as well as the follow-up performed annually since 1994.

PRESENTATION OF SITE

In 1987, a treatment center against cancer was built with under floor of a hospital building. For this type of site having to accommodate a particle accelerator, a very detailed attention must be given to the means of protection against γ–rays. Thus, to protect the personnel from the radiation, a protection by high-density concrete having a density higher than 3.5 is recommended. The manufacture of concrete is generally carried out thanks to the use of dense natural aggregates (barite, hematite) or of ferrous waste. In the majority of the treatment rooms, concrete protection contains barite whereas, in the studied case, hematite aggregates were used.

High-density concrete, of 32 MPa strength, was manufactured in a concrete mixing plant using hematite aggregate from Brazil (size ranges of 0/8 and 8/26 mm), French blended portland cement (type CEM II/B 32.5 R), proportioned with 350 kg/m^3, and water. It was consolidated by vibration in the zones subjected to the direct radiation that is two walls (thickness : 0.50 and 1.60 m) and a part of the ceiling (thickness : 1m). Thereafter, an impermeable paint was put inside the room.

TECHNICAL MISSION OF 1991

Presentation and Location of the Defects

At the time of our first intervention, in 1991, the report inside the room was the following :

- presence of many craters and pop-outs visible on the parts corresponding to the high-density concrete (walls and ceiling). Swelling zones, from 2 to 4 cm in diameter, corresponded in the majority of the cases to the formation of a cone which separated easily. At the bottom of the crater (depth ranging between 2 to 10 mm) appeared a bloody red aggregate (photo 1). In certain cases, translucent gels were associated with the pop-out (photo 2) ;
- presence of some cracks on the walls (horizontal crack in high partly for a wall and in median partly for the other) and on the ceiling by which exudations of gel ran out locally. Their openings generally exceeded 200 μm ;
- no visible defect on the parts made with ordinary concrete.

At the outside of the room, on the only accessible high-density concrete wall, one observed neither craters, nor pop-outs. However, a dense grid of microscopic cracks, reproducing the wire mesh (present only outside), was visible just as was visible the partly high crack which thus proved to be crossing.

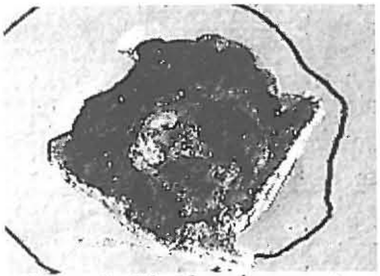

Photo 1 : Bloody red aggregate
at the bottom of the crater

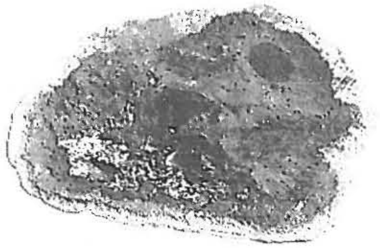

Photo 2 : Gel visible on the crater

Taking Away and Analysis Defects

Several samples were obtained from inside and outside the room by scraping (gels and pop-outs) and by coring (7 cores for examination with a diameter 50 mm and depth 80 mm and 40 micro-cores for density measurement with a diameter 10 mm and depth 100 mm). Samples were tested for apparent and absolute density, observations by optical microscopy and scanning electron microscopy (with qualitative analysis of the elements by X-spectrometry EDS) and quantitative chemical analysis by microsounder. Moreover, minerals characterisations by X-rays diffraction and petrographic analysis on thin sections by optical microscopy were carried out. Lastly, an elementary test of reactivity in controlled environment was conducted.

Measurements of Density - On the whole of the wall, apparent densities of high-density concrete generally varied from 3300 to 3650 kg/m^3 with however some values lower than 3.00. Thus, in many zones, high-density concrete had a density lower than that indicated in the schedule of conditions. There existed in this hardened concrete considerable variations of density due either to problems of quality of material or proportioning during the manufacture phase, or with a very strong segregation at the time of the casting. Taking into account the absolutes densities measured (varying from 3800 to 4200 kg/m^3), average porosity of the hardened concrete could be estimated at 15%.

Microscopic Aspect and Chemical Analysis of the Defects - On the fresh surface of pop-out, it systematically appeared smooth gel, a thickness greater than 20 µm, which seemed to run out starting from the central crater (photos 3 and 4). Moreover, some particular crystallisation in shape of massive needle, more fine needle, rosette-like crystals, spherical concretion or of « tree structure » are visible on gel (photos 5, 6, 7, and 8). Qualitative chemical analysis carried out by spectrometry X (EDS) showed that the gel contained primarily silicon and potassium, whereas concretions (spheres and rosette) contained also calcium. The composition of the needles corresponded to a ferruginous ettringite (Table 1).

TABLE 1 : Chemical Elements Present

Observed zone	Principal elements	Secondary elements
Gels	Si, K	Na, Fe
Polymorphous products	Si, Ca, K	Na, Fe
Needles	Ca, S, Al	Fe
Rosette-like crystals	Si, Ca, K	Fe

Photo 3 : Gel from the central crater

Photo 4 : Smooth gel

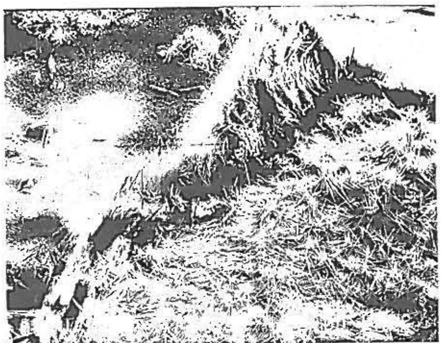

Photo 5 : Needles of ettringite visible on the gel

Photo 6 : Rosette-like crystals visible on the gel

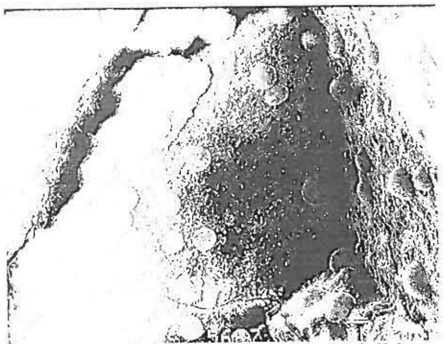

Photo 7 : Spherical concretion visible on the gel

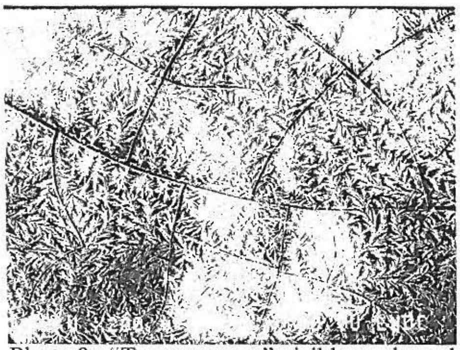

Photo 8 : "Tree structure" visible on the gel

Mineralogical Analysis of Concretes and Aggregates (X-rays diffraction) - The diffractograms, carried out on a part representative of the concrete, highlighted mainly peaks due to aggregates (hematite, quartz, chlorites, micas, and feldspars) and, in smaller proportions, to cement hydrates (portlandite and ettringite) or to secondary compound of blended cement (calcite). These diagrams thus showed that a different aggregate had been used in small proportion or had contaminated the high-density aggregates. It was probably a quartz river sand.

Mineralogical analysis of high-density aggregates taken in the heart of the concrete showed that they consisted of hematite and crystallised quartz. The mineralogical analysis of the aggregates found in bottom of crater showed that they were made up either only of goethite, or of a mixture of goethite, hematite, and quartz.

Petrographic Analysis - Microscopic observation of aggregates, in thin sections produced from the heart of the concrete, had highlighted, in addition to the hematite aggregates, of small undulatory extinction quartzes or fractured quartzes. Quartz was also visible inside the iron ore, either in insulated grains, or in interconnected grids of cryptocrystalline silica.

Microscopic observation of reactive aggregates, present in bottom of crater, had shown that they were composed of iron ore present at several levels of hydration (hematite Fe_2O_3 of brown colour, goethite Fe_2O_3 H_2O of red colour and limonite $2Fe_2O_3$ $3H_2O$ of orange colour) as well as quartz present in the form of interconnected grids. Limonite, not presenting quite clear crystallisation, could not have been detected with X-rays.

Analysis of Swelling Aggregates - This analysis had made it possible to note that the aggregates present in bottom of crater could contain 3 to more than 63% of iron and 46 to less than 5% of silicon. The microscopic observation of a polished section of one of these aggregates, in backscattered electron mode (BSE), made it possible to distinguish the hematite ranges (in black) separated by a siliceous interstitial phase (in white) (photo 9). The volume percentage of silica finely crystallised, was, in this case, very significant.

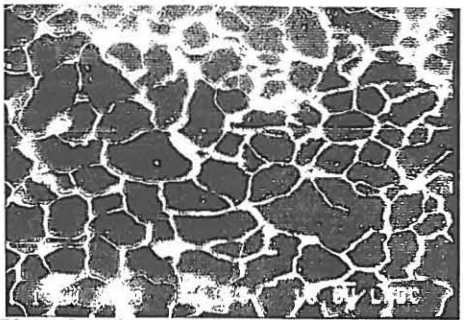

Photo 9 : Observation of a reactive aggregate (silicon in white, hematite in black)

Reactivity of the Concretes in the Presence of Water or Sodium Hydroxide - To measure the potential reactivity of the concretes, the apparently healthy cores had been placed either in sodium hydroxide, or in water at 40°C. Samples placed in sodium hydroxide did not present visible degradation after two weeks of immersion and return to normal environment whereas cores in water did crack after drying. Observation of fissured zone in electron microscopy had shown the presence of massive silico-calco-alkaline gel. Same manner, on a core taken in a healthy zone and preserved at ambient temperature and moisture, one saw an exudation of gel appearing around an hematite aggregate which led to its disintegration. Chemical analysis of this gel showed that it was also silico-calco-alkaline.

Conclusions of the Technical Expertise

Two types of reactions could have been highlighted as early as 1991 in this high-density concrete :

1 - A hydration of hematite which is being converted into goethite and into limonite with increase in volume (increase being able to reach 600%, Dolar-Mantuani 1981). This swelling reaction generates stress which result in the appearance of pop-outs with the

systematic presence of a reddish aggregate at the bottom of the crater (color due to the high degree of hydration of the iron ore).

2 - An alkali-reaction which had already caused formation of gels, starting from siliceous inclusions of hematite aggregates. Those had been able, by places, but in a very limited way, to run out outside the walls. This gel had an initially silica-alkaline composition, and seemed to be non expansive, but it appeared evolutionary and tended to crystallise by including calcium in its structure. Some formations of needles of ferruginous ettringite had also been highlighted. This alkali-silica reaction involved aggregates classified as not reactive (they contain on average less than 2 % in mass of quartz, but taking into account the differences in density, the volume proportion in reactive silica is high) and occurred in a low alkali concrete (lower than 3 kg/m^3). It will thus be advisable to think, when one deals with very variable density aggregates, light or high-density, as well with the mass contents as volume proportions.

The cracks observed on the wall seemed to rise from the differences in shrinkage in the concrete due to heterogeneity of density (problem of composition and segregation) and/or to high water contents at the time of the placing (related certainly on high porosity and pollution of surface of the high-density aggregates). They did not appear to bind to the surface phenomena observed.

Possible Influence of the Radiation - The outstanding facts of this study were on the one hand the speed with which the disorders had appeared, and, on the other hand, the presence of these disorders only in the zones subjected to the bombardments of the γ-rays. Indeed, no swelling appeared on the high-density concrete outside the room and, except for the defects of surface, no other transformation was visible initially in the heart of cores taken inside the room. The presence of an impermeable painting inside and the permanent temperature of 22°C could can be to explain the difference in reaction between the interior (with high moisture) and the outside (with low moisture) of the room (Miyagawa, 1992). But, it was possible as the bombardment by the γ–rays is at the origin of the hematite - goethite - limonite transformation and of the silica gel flow (dissociation and combination of reactives phases due to electronic excitation and vibration) like electric or magnetic field following certain authors (Natesaiyer et al., 1986 ; Page et al., 1992).

Proposals for a Follow-up of the Work - The tests having shown that the reactions which occurred in the high-density concrete were surface but evolutionary, we proposed to the building owner to equip the interior wall to make regularly measurements of deformations and visual follow-up of the evolution of the surface defects. Taking into account the surface aspect of the defects, cost which would have generated the demolition and the rebuilding of the room and especially of the absence of treatment for the patients during the work, this solution was retained.

FOLLOW-UP OF THE WORK SINCE 1994

Equipment of Monitoring

In 1994, a wall was entirely equipped with steel balls stuck on the surface according to a squaring of mesh of 20 cm (approximately : 150 balls on the wall). Deformation measurement be take horizontally and vertically (more than 250 measurement) with a comparator with 0.002 mm precision. 13 deformation gauges, more sensitive, have been laid out straddling on the crack, on some area of swelling and on some healthy concrete (reference). A cartography of the whole of the defects was carried out. Photographs of the wall were also taken to follow the evolution of the defects.

Frequency of Measurements

The wall having been protected by a removable plaster partition, quarterly measurements of the gauges deformations are taken without dismounting the partition (lasted = ½ H). Annually, the partition is dismounted and complete measurements and observations are carried out (lasted 1 day and 1/2). Examples of these monitoring on a part of the wall are given on Fig. 1 and Fig. 2.

PANNEAU 1						
A1	0,300	B1	-0,180	C1	0,114	D1
-0,018		0,096		0,012		0,132
A2	0,054	B2	0,078	C2	0,108	D2
-0,300		-0,252		-0,360		-0,300
A3	-0,030	B3	0,000	C3	-0,078	D3
0,024		-0,072		0,114		-0,006
A4	0,204	B4	0,000	C4	0,018	D4
0,114		-0,264		0,060		0,126
A5	-0,036	B5	-0,012	C5	0,096	D5
0,240		0,192		0,132		0,000
A6	0,210	B6	0,012	C6	0,168	D6
0,096		0,126		0,132		0,120
A7	0,102	B7	0,168	C7	0,108	D7
-0,384		0,168		0,162		0,222
A8	0,222	B8	0,108	C8	0,108	D8
0,186		0,144		0,198		0,162
A9	0,144	B9	0,150	C9	0,204	D9
0,120		0,198		0,156		0,120
A10	0,240	B10	0,108	C10	0,084	D10
0,198		0,060		0,156		0,264
A11	0,114	B11	0,132	C11	0,144	D11
0,096		0,174		0,252		0,072
A12	0,126	B12	0,054	C12	0,198	D12

Fig. 1 : Surface deformation en µm/m

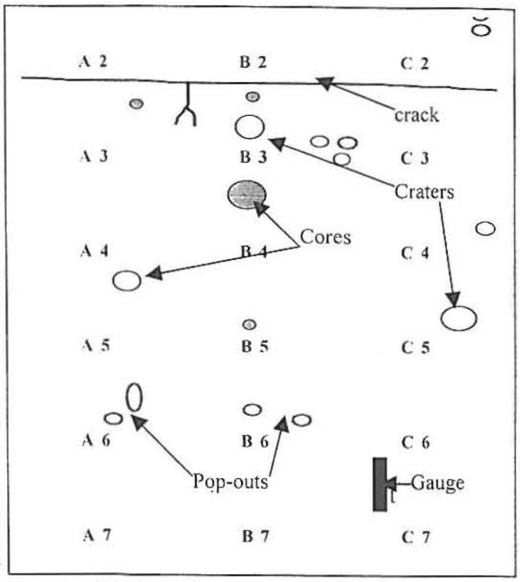

Fig 2. : Observations of defects

Results of the Follow-up

Dimensional Variations on the Surface - Measured variations are weak and not very evolutionary. Maximum departure from the initial state of 1994 was -0.45 to +0.45 mm/m in 1995, -0.38 to +0.84 mm/m in 1996 and -0.41 to +0.98 mm/m in 1999.

Dimensional Variations of Defects and Cracks Opening - The follow-up of the deformations realised by the gauges show that the defects located on the wall are stabilised but that the cracks continue to open regularly (+ 200 µm in two years) (Fig. 3).

Visual Follow-up of the Defects - Some defects continue to appear on the surface but the increase is now weak. These defects appeared as small pop-outs very localised, similar to the first appeared disorders.

Microscopic analysis of the defects - The microstructures of the new pop-outs observed are apparently the same ones as those observed in 1991. An enrichment of gel in calcium is however notable (photo 10) just as a greater proportion of ettringite is observed (photo 11).

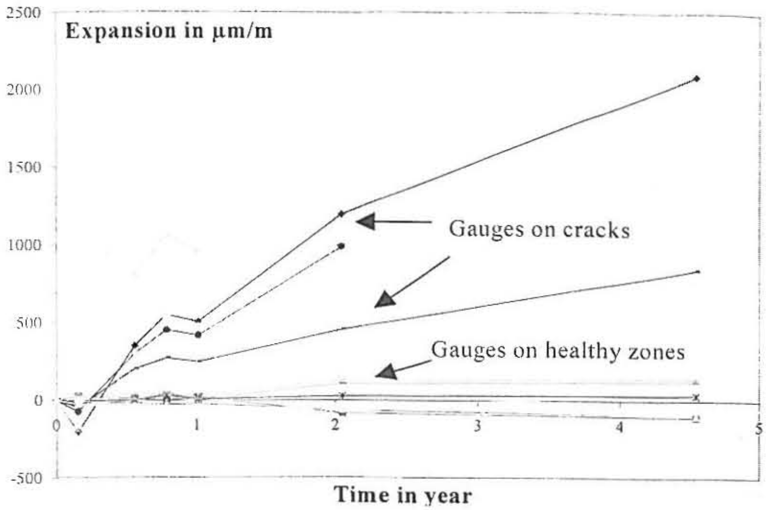

Fig. 3 : Gauges deformations

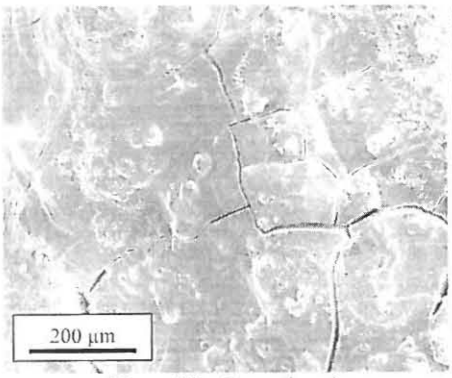

Photo 10 : Smooth gel

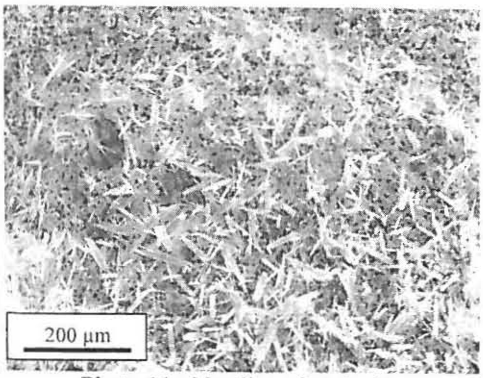

Photo 11 : Needles of ettringite

Comments

The follow-up of the surface defects did not make it possible to highlight a significant evolution of the high-density concrete wall. It thus seems that the majority of the reactions of swelling proceeded very quickly (the first three years) what is contrary with the known kinetics of the alkali-silica reactions or hydration of the iron ore (Bérubé et al, 1992). The assumption of an acceleration of the reactions due to the γ-rays is thus always valid. Moreover, it is possible that the follow-up of the deformations on the surface of the high-density concrete did not make it possible to highlight notable dimensional variations whereas, in same time, the opening of the cracks increases. The problem of the dimensional follow-up is thus posed. It is all the more significant when one must, as in this work, to follow a massive wall (thickness of 1m60), not very accessible.

Tests Envisaged

Taking into account advanced knowledge in the field of alkali-silica reaction and the validation of many laboratory tests (Thaulow et al., 1992, Larive, 1998),it is envisaged to carry out soon accelerated tests of residual swellings on cores taken in the wall, more in the possible heart.

CONCLUSIONS

The first analysis carried out in 1991 highlighted two simultaneous causes of degradation being able to explain the disorders appeared on a high-density concrete in less than 3 years:

- a localised transformation of the aggregates of hematite into goethite and limonite which is accompanied by an increase in volume ;
- a alkali-silica reaction occurring between quartz inclusions present in the iron ore and the alkaline ones of cement. The gel observed contains little or no calcium. On the other hand, calcium is found on the level of crystallisation in the form of rosette-like crystals or other polymorphous products. Some needles of ettringite are also observed.

Thus, the doubly reactive character of this type of aggregate was highlighted. However, taking into account the very fast kinetics of appearance of the disorders, of the surface character of the disorders observed and their localisation in the zones of bombardment by the γ-rays, it is extremely possible that the electronic bombardment is an accelerating factor of the observed reactions. These aggregates being able to be used in the storage of nuclear waste, it would certainly be advisable to undertake studies to confirm or cancel the stability of the high-density concretes in this type of use.

Lastly, the follow-up of the work carried out since 1994 does not show very significant evolution of the facing whereas the cracks continue to open. This poses the problem of techniques monitoring to be implemented to evaluate degradation evolution and the difficulty of interpretation of the results to manage to predict the lifespan of the structure.

REFERENCES

Bérubé, M.A., and Carles-Gibergues, A, 1992. "La durabilité des bétons face à l'alcali réaction". *La Durabilité des Bétons*, Presses de l'ENPC, pp. 285-350.

Dolar-Mantuani, L., 1981. "A petrographie and technological evaluation". *Handbook of concrete aggregates*. Noyes publications, Park Ridge, New Jersey, USA.

Larive, C., 1998. "Apports combinés de l'expérimentation et de la modélisation à la compréhension de l'alcali-réaction et de ses effets mécaniques". *Rapport de recherche OA28*, Laboratoire Central des Ponts et Chaussées, France.

Miyagawa, T., Inoue, S., Fujii, M., and Uehata, N., 1992. "Effect on concrete surface treatment on expansion due to alkali-silica reaction". *9th International Conference an Alkali Aggregate Reactions in Concrete*, London, U.K., pp.660-667.

Natesaiyer, K., and Hover, K.C., 1986. "Investigation of Electrical effects on alkali-aggregate reaction". *7th International Conference an Alkali Aggregate Reactions in Concrete*, Ottawa, Canada, pp.466-471.

Page, C.L., Sergi, G., and Thompson, D.M., 1992. "Development of alkali silica reaction in reinforced concrete subjected to cathodic protection". *9th International Conference an Alkali Aggregate Reactions in Concrete*, London, U.K., pp.774-778.

Thaulow, N., and Geiker, M.R., 1992. "Determination of the residual reactivity of alkali silica reaction in concrete". *9th International Conference an Alkali Aggregate Reactions in Concrete*, London, U.K., pp.1050-1058.