At age of one day.

After five years.

Figure 4: The expanded perlite mortar bars (1x1x10 inch)

EXEMPLES OF DETERIORATION BY ALKALIS IN ITALIAN CONCRETE STRUCTURES

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1. INTRODUCTION

The so-called alkali-aggregate reaction (AAR) constitutes a serious problem in several countries, being normally related to anomalous expansion of concrete, causing fissuration, loss of strength and, in some cases, complete destruction of the concrete itself. As it is well known, this reaction takes place between alkali cations and hydroxyl ions from concrete pore solutions and amorphous or cryptocrystalline silica from some grains of aggregate /1/.

Fortunately, such phenomena are very infrequent in Italy: the only exemples reported by technical literature concern some industrial pavements situated in the regions bordering on the Adriatic Sea, as Romagna, Marches and Abruzzi /2/.

Recently, however, some parts of an 8 years old concrete structure were found highly fissured. The cracking pattern, caused by the growing of expansive gel inside the concrete, together with the results of chemical and petrographical analyses, carried out respectively on the aggregate, the reaction products and the concrete, led to the hypothesis of AAR. It has to be remarked that the building is situated in Lower Molise, slightly south of the area considered by /2/.

Keywords: aggregate; alkali-aggregate reaction; deterioration of concrete.

2. OBSERVED DECAY OF STRUCTURAL CONCRETE

The building appeared degraded after about 8 years since the casting of concrete structures; on the other hand, it is known that AAR can produce its negative effects only after about 5 or 6 years /3/.

The cracks assumed a different pattern according to the fact that restrained or unrestrained concrete were affected by AAR. Deep cracks, more or less parallel to reinforcing bars, could be seen in reinforced concrete colums; typical, randomly distributed, map cracks had formed on the surface of unrestrained massive concrete blocks (fig. 1).
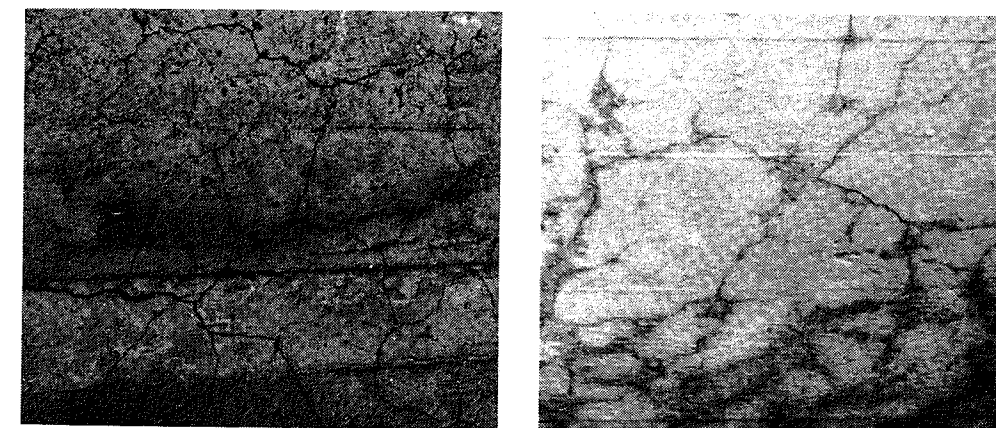

Fig. 1: left, right. Two aspects of map cracking on massive concrete blocks.

On cracking surfaces inside the concrete, the presence of abundant gel could be observed: the gel showed a tendency to expand out of pores, after having saturated them; besides, several aggregate grains, clearly attacked by AAR, were visible to the naked eye (fig. 2). Also, from SEM examination of cracking surfaces, the finest fractions of the aggregate resulted to have undergone a similar attack (fig. 3).

The presence of gel, together with altered grains in a fissured concrete, are evident signs of AAR /4/.
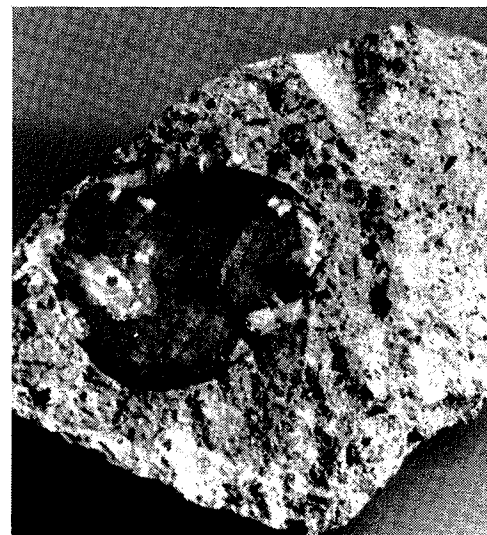

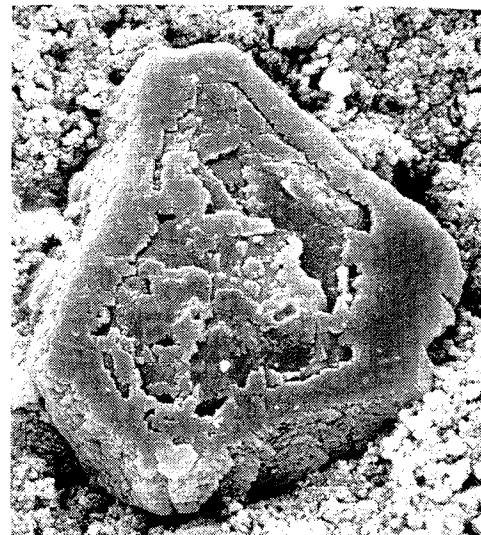Fig. 2. Altered grain of chert, showing dark rim and reaction products.　　Fig. 3. Altered sandsize grain as seen by SEM (2400 X).

3. FACTORS AFFECTING ALKALI-AGGREGATE REACTION

It is known that AAR is influenced by the following factors /4/, /5/:
a) reactivity of aggregate;
b) alkaline content of cement;
c) environmental conditions (humidity and temperature).

3.1. Reactivity of aggregate

Several concrete samples were taken by drilling (core diameter = 100 mm), from columns and footings of the building. The length of the single core was variable, depending on the degree of fissuration (fig. 4).

Some medium fissured cores were selected, in order to separate the aggregate elements from the surrounding cement paste. Petrographical, diffractometer and chemical analyses were performed on the aggregate, for evaluating its potential reactivity.

3.1.1. Petrographical analyses

From the geological point of view, the aggregate comes from comminution of recent and actual alluvia, deriving essentially from erosion of Cretaceous calcareous formations. Such limestones, outcropping along the Adriatic side of the Apennines, include a lot of nodules, lenses and thin beds of chert. Consequently, the aggregate quarried from alluvial coarse deposits is formed mainly by calcareous grains, sometimes marly, with a variable amount of sili

Fig. 4. Concrete core taken from the structure, showing deep cracks.
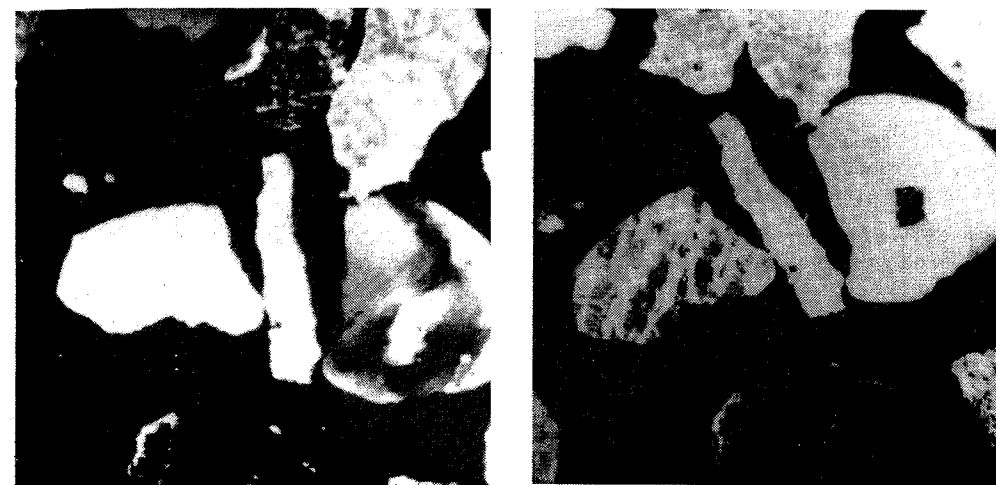

Fig. 5: left, right. Undulatory extinction (angle > 20°) in sandsize grains of strained quartz.

ceous grains (chert cobbles).

Besides, the calcareous fragments often include some granules of quartz, whose crystalline lattice had been strained by tectonic stresses, as put in evidence by the undulatory extinction angle, varying from a few degrees up to more than 20° (fig. 5). It is known that quartz grains with extinction angle more than 15° are potentially reactive /5/. Also, SEM analyses carried out on the finest fraction allowed to recognize some grains of partially altered feldspars.

Up to date, petrographical analyses are the most reliable methods for ascertaining the reactivity of aggregates to AAR /5/.

3.1.2. Diffractometer analyses

On the basis of diffractometer analyses, the altered elements resulted to be composed mainly by calcite, with small amounts (2 ÷ 3 %) of quartz and some feldspars and clay minerals. Both cryptocrystalline or highly strained quartz and feldspars are susceptible to be attacked by relatively concentrated alka-

line solutions /6/, /7/.

It should be remembered that diffractometer analysis allows to recognize only crystalline phases; therefore, the eventual presence of amorphous silica should be put in evidence by other analytical procedures (e.g. thin sections and SEM analyses).

3.1.3. Chemical analyses of aggregate

The aggregate was preliminarly subdivided into four granulometrical classes, then analyzed with the main scope to determine its content in sulfates; the results are reported in table I. It is evident that the concrete deterioration cannot be imputed to an hypothetical presence of sulfates coming from the aggregate.

Table I. Results of chemical analyses on aggregate.

Grain size interval	Sulfates as SO_3 (%)	Insoluble residue (%)
0.07 ÷ 5 mm	0.05	10.91
5 ÷ 8 mm	0.03	4.24
8 ÷ 20 mm	0.02	5.11
20 ÷ 30 mm	0.04	4.36

In order to evaluate the potential reactivity of this aggregate, the rapid method proposed by ASTM (C 289-71) was adopted. The values obtained for the different granulometrical fractions are reported in fig. 6: on this basis,
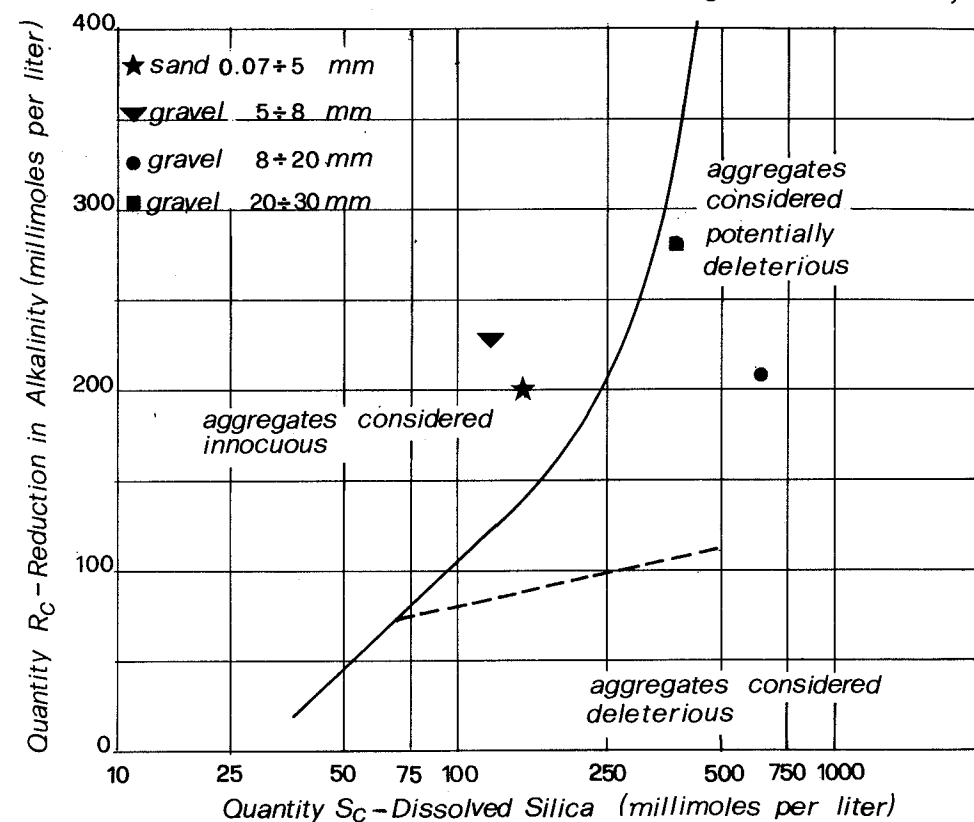

Fig. 6. Reactivity of aggregates according to ASTM C 289-71.

only coarse gravel (8 ÷ 20 and 20 ÷ 30 mm) should result potentially deleterious. It is interesting to remark that similar results were obtained by testing fresh aggregates taken from the same quarry from which had been taken the aggregates used for the building.

Several authors (e.g. /8/) are in doubt about the reliability of such test, that was formerly proposed for sands, but does not seem proper for the so-called "polyphased" aggregates. In fact, aggregates that had been considered innocuous according to this chemical test, resulted long-term reactive for structures built up in humid environment.

3.2. Alkaline content of cement

From chemical analysis on cement (declared as "Portland 425"), the alkaline content resulted as follows:
- Na_2O = 0.24 %,
- K_2O = 1.18 % ,
corresponding to an equivalent Na_2O = 1.01 %.

According to ASTM specifications, the equivalent Na_2O for a Portland cement to be employed with potentially reactive aggregates should be lower than 0.6 %. However, most of researchers differ with this value, although they don't agree each other about the limit value not to be exceeded (for instance, /9/ proposed 0.8 %). In any case, the equivalent Na_2O content found by analyses is superior both to ASTM limit and to the limit values proposed by most researchers.

3.3. Environmental conditions

The building considered in this work is situated in a small alluvial plain close to the Adriatic coast. As it corresponds to a marsh area, the foundation soil is mostly formed by clayey silt with traces of peat. Besides, the phreatic level is varying depending on the seasonal rainfall regime, so that part of the structure undergoes alternate periods of wetting and successive desiccation. These environmental conditions are the most favourable for developing of AAR /3/, /4/, /5/.

4. ANALYSES ON CONCRETE CORE SAMPLES

Several core samples were taken from the structure: only a few of them seemed sufficiently intact, while the others appeared more or less cracked, so that reliable mechanical tests were not possible (see fig. 4).

4.1. Chemical, physical and mechanical properties

The average results of chemical analyses on concrete cores are reported in table II.

Table II. Results of chemical analyses on concrete samples.

Chemical determination	%	Chemical determination	%
Ignition loss	30.10	Na_2O	0.26
CO_2	29.08	K_2O	1.02
SiO_2	20.06	SO_3	0.49
Al_2O_3	0.40	Chlorides	0.01
Fe_2O_3	3.62	Insoluble residue	16.67
CaO	42.93	Soluble silica, according	
MgO	0.86	to UNI 6505-73	4.59

The analytical data confirmed that the aggregate was mainly formed by calcareous grains, with subordinate content of siliceous grains.

The sulfate content corresponds to a concrete dosed with 350 ÷ 400 kg/m³ of cement. However, the soluble silica content is too high to be originated solely from the silicates of cement (C_2S and C_3S); likely, part of soluble silica could come by dissolution from the reactive aggregate. Besides, the equivalent Na_2O (1.19 %) exceeds the limit values computed according to /9/, that should be 0.75 and 0.86 %, respectively for 400 and 350 kg/m³ of cement in the concrete.

Some cores taken from medium to poorly degraded parts of the structure allowed some physical and mechanical properties to be measured (see table III).

Table III. Results of physical and mechanical tests on concrete cores (diameter = 100 mm; length ≃ 200 mm).

Core no.		1	2	3	4	5	6	7
Density	(kg/m³)	2310	2290	2390	2370	2280	2280	2280
Water absorption	(%)	2.9	3.6	1.5	1.9	3.0	3.2	4.7
Compression strength	(MPa)	30.9	33.4	53.0	41.9	13.5	14.5	14.6

The average density (2314 kg/m³) is rather satisfactory; concerning the water absorption and the compressive strength, the measured values are randomly scattered, as a consequence of micro- or macrocracks.

4.2. Induced acceleration of AAR

In order to reproduce the phenomenon of AAR in the laboratory, some non-fissured 200 mm long cores were stored under water at 20°C for several days until saturation, then measured to obtain reference lengths; subsequently, they were placed vertically over water at 38°C, with 80 ÷ 90 % of relative air humidity. The specimens were measured at time intervals; the so-determined length changes are reported vs. time in fig. 7.

After about 2 weeks of such a treatment, local pop outs appeared on the surface, together with outcoming white gel at the grain ‑ cement paste interface and with cracking of cement paste itself (fig. 8); also, the expansion of gel
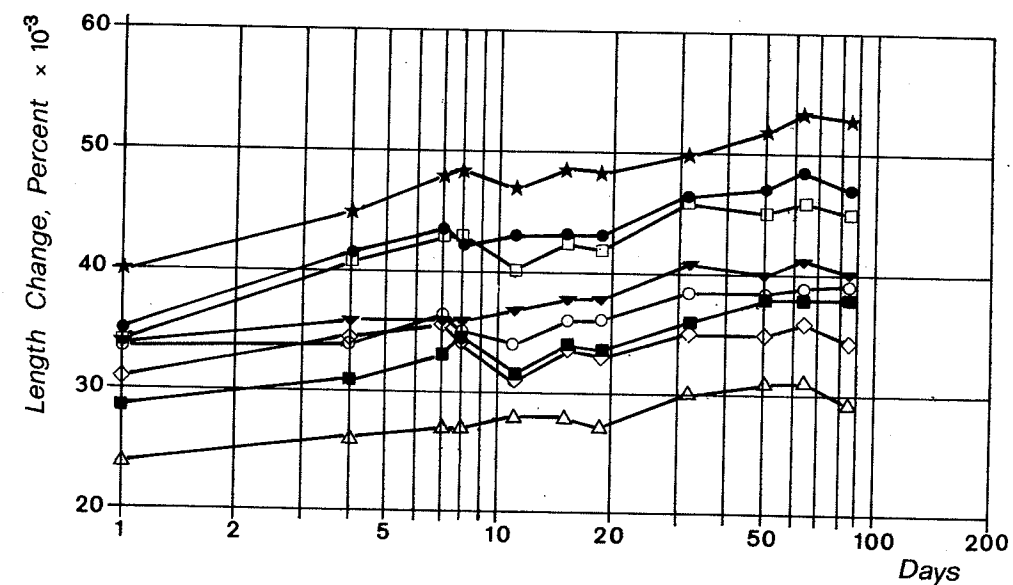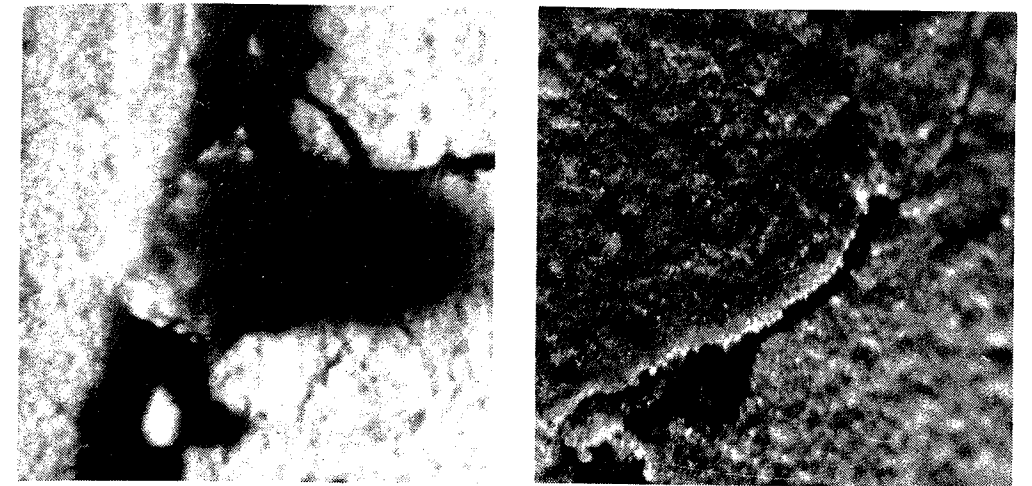

Fig. 7. Expansion of concrete cores vs. time.

Fig. 8. From left: pop out of an aggregate grain, reaction product and cracked cement paste.

Fig. 9. Cracking of aggregate grain.

caused grain cracking (fig. 9). The length change of some specimens reached 0.04 ÷ 0.05 % within about 3 months; these values are much higher than limit values accepted by the Canadian Standard Association (CSA, A23.2-14A) for footings in a humid environment like the examined in this case history.

4.3. Analyses on reaction products

By SEM analysis, the reaction products appeared as gels, fissured by shrinkage (fig. 10). Their average chemical composition was determined by AAS and is reported in table IV.

Table IV. Average chemical composition of reaction products (percent).

Ignition loss	CO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
15.93	2.70	66.46	2.74	0.44	6.47	2.26	traces	1.23	4.15

Likely, the prevalence of silica is due to solubilisation of reactive silicic fractions of the aggregate, by attack of OH^- ions coming from the alkaline pore solutions in cement paste.

AAR became evident with a dark rim all around the aggregate grain and with white deposits inside the fissured grain (see fig. 2); according to /7/, the dark rim could be imputed to the presence of Fe.

According to microprobe analyses, the composition of reaction products was varying by zones, the dark rim being formed mainly by Si with minor amounts of K, Ca, Fe, the white deposits inside the aggregate showing increase of K and decrease of Si and Ca; besides, the gel deposited into pores and cracks of cement paste was enriched in Ca and impoverished in Si and K (with respect to gel formed on the aggregate surface).

As stated by thin section and SEM optical analyses, the interstitial alkaline solution attacked preferably the more or less calcareous cobbles including amorphous or cryptocrystalline silica (fig. 11); the rare feldspatic grains and some fine crystallized quartz grains were also attacked by AAR, even if the latter did not show any undulatory extinction.
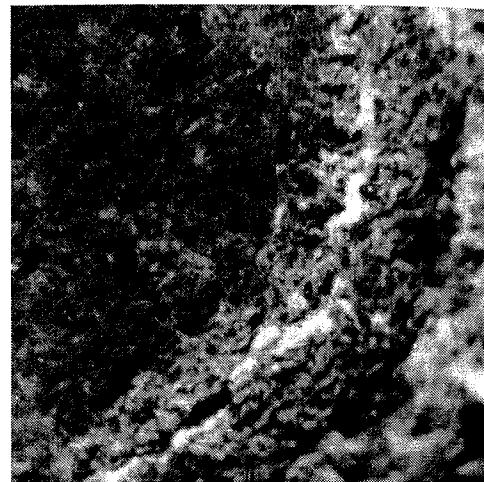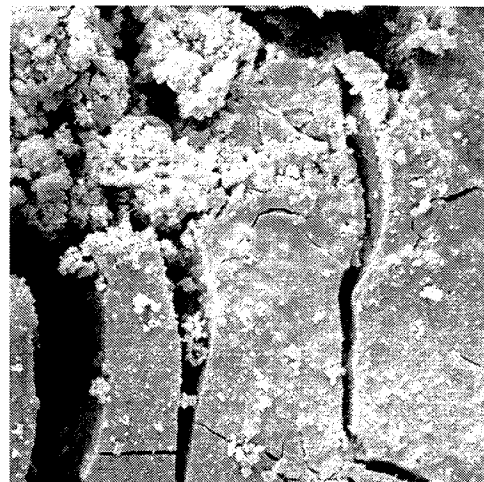
Fig. 10. Jelly deposit of reaction products, fissured by shrinkage.(400 X).

Fig. 11. Enlarged view of dark rim on
a marly limestone cobble.

5. CONCLUSIONS

Detailed investigations on all concrete samples allowed to conclude that AAR
was the most probable cause of the building decay, for the following reasons:
- cracking of concrete structures in humid environment after 8 years since
  concrete casting;
- deposit of jelly reaction products on crack surfaces, in the concrete mass
  and in grains of an aggregate defined as "potentially deleterious" by chem-
  ical and petrographical analyses;
- finding, inside the concrete mass, altered siliceous grains and aggregate
  grains showing outer dark rim and inner white zone;
all these, reliable signs of alkali-aggregate reaction /8/.

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INVESTIGATION FOR NATURAL REACTIVE AGGREGATES IN
GRAVEL ALLUVIUM OF YANGTZE RIVER BASIN

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ABSTRACT

Multiple purpose projects were constructed and being constructed for the deve-
lopment of water resource of the Yangtze, China. The main hydraulic structures
are largely concrete dams. Some of these concrete dams were constructed with
natural construction material containing reactive aggregates. For inhibitting
the damaging action of the deleterious reaction of reactive aggregates, preli-
minary investigations were conducted for geographical distribution within the
Basin and detailed studies measures taken, were made for mitigating, if neces-
sary. A comprehensive account of above-mentioned studies is given in the paper.

INTRODUCTION

The Yangtze River is the longest river in China and is the third largest of the
world. In order to develop its abundant water resources, it is essential to
investigate the reactive aggregates in gravel alluvium of the main stem and
tributaries of the upper and the middle reaches of the Yangtze River and take
samples from the above-mentioned areas for tests. Considerable work has been
done and this paper will describe the classification, the distribution and the
test result of the reactive aggregates in that area.

DISTRIBUTION OF NATURAL REACTIVE AGGREGATES

In the past thirty years, reactive aggregates have been studied in sand and
gravel deposits in the main stem and tributaries of the upper and the middle
reaches of the Yangtze River, including Ganjiang of The Poyang Lake Water Sy-
stem, the Dongting Lake Water System, Hanjiang, the Sichuan Water System and
the reach of Jinshajiang below Shigu, and samples have been taken from the
above-mentioned areas for tests with a view to finding out the reactive aggre-
gates that should be used in concrete. Here are some results of the study.

(1) According to Xu Huarong's classification, the reactive aggregates in sand
and gravel deposits fall into two kinds, the kind of alkali-silica reaction
such as flint and its varieties (agate and jasper) and the kind of alkali-sili-
cate reaction such as rhyolite, trass, andesite, dacite, breccia. In addition,
some siliceous slates are found. Photos show the appearance and microstructure
of the reactive aggregates.

(2) The distribution law of the reactive aggregates is quite clear. The natu-
ral reactive aggregates in Tuojiang and the main stem and tributaries of the
Yangtze River below Tuojiang are mainly composed of flint with the exception
that a small amount of agate is found in particular area and a small amount of
rhyolite and trass is found in the Gezhouba area just below the outfall of the
Three Gorge and a considerable amount of siliceous slate is found in Hangjiang
and Yuanjiang area. The proportion of flint amounts to 18%. The reactive aggre-
gates in the main stem and tributaries of The Yangtze River above Tuojiang are