ALKALI-SILICA REACTIVITY OF SOME ITALIAN AND EUROPEAN FLINTS

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ABSTRACT

Studies carried out on the alkali-silica reactivity of Italian and other European sands and gravels - whether based on mortar-bar tests (ASTM C 227) and similar, on the chemical method (ASTM C 289), or on case histories comparison - often showed marked differences in reaction intensity of aggregates having, according to petrographic examinations, similar contents of reactive materials (mainly flint). Moreover, flint content being equal, the reactivity of Italian aggregates appeared far lower than it resulted for English or Danish ones. To explain such anomalies, a study was started on the recrystallization degree of flints commonly occurring in Italian alluvial deposits. These flints normally come from nodules or tabular bands in limestones whose age varies from Triassic to Miocene; the samples to be studied were collected in rocks outcropping in central and southern Appennines. To verify the existence of a correlation between the reactivity of flints and their age, a series of different analyses was carried out, particularly centered on optical methods (petrographic examination), chemical methods (ASTM C 289), physical methods (microhardness) and X-ray diffraction methods; control samples were also collected from rocks and alluvial deposits in Great Britain, Netherlands, Germany, and Denmark. In total, over 30 samples were tested, but the analysis carried out did not show clear distinctive features between the highly reactive flints and the low reactive ones. The existence of correlation between the geological age and the alkali-silica reactivity was not established.
Keywords: AAR,, age, crystallization degree, flint.

INTRODUCTION

The alkali-silica reactivity of a large part of Italian sands and gravels appears very low, mainly if compared to other European deposits with a very similar flint content (flint being the main, and often the unique, reactive mineral) (Barisone 1984; Barisone et al. 1986; Barisone & Restivo 1992a; Baronio 1984; Christensen et al. 1983; Lenzner & Ludwig 1978; Palmer 1981; Rossetti et al. 1988).

It was reported that the reactivity of certain flints in the United Kingdom is strictly connected with porosity (Rayment 1992), and particularly with the thickness of a porous rim (the "cortex") that usually surrounds the flint pebbles (especially those coming from limestones, the cortex often corresponding to the original contact zone between calcite and opal).

It is, on the contrary, not yet clear if and how the crystallization degree of original opal in flints having different geological ages is an important parameter - as it should be theoretically (Andersen & Thaulow 1990; Barisone & Restivo 1992b) - in influencing the degree of reactivity; a correlation between reactivity and age will be useful also in

practice, permitting a preliminary screening of potentially reactive alluvial deposits on a geological basis.

In order to investigate this problem, 20 samples of Italian flints of various geological ages (ranging from lower Jurassic to upper Miocene) were collected in 10 different localities, mainly from nodules or tabular bands occurring in limestones and marls outcropping in the central and southern part of Appennines range; to better evaluate the influence of the age on recrystallization and potential reactivity, 11 control samples were also collected from deposits in Great Britain (4 samples, nodules in limestones and pebbles in sea beaches), Netherland, Germany and Denmark (7 samples, pebbles in old and recent sea beaches). Italian and European localities concerned by the sampling are shown in Fig.1.

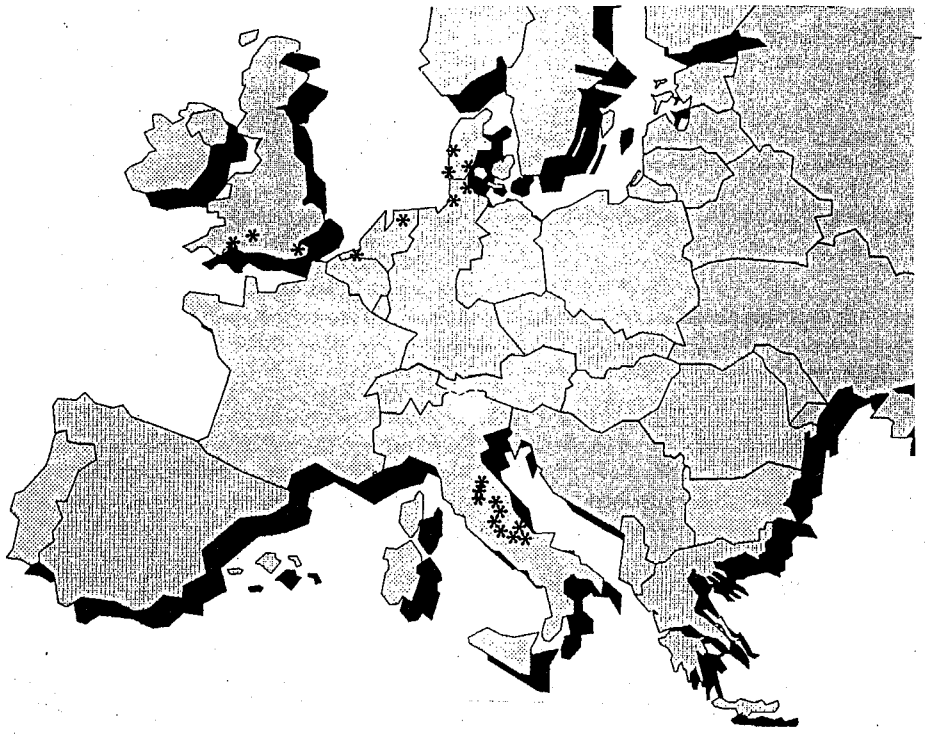

Fig.1 Locations from which the samples were collected

Italian samples were collected partly in areas known for the presence of reactive materials (case histories and ASTM C 227 tests), partly in areas where no alkali-silica reaction cases were ever signaled; the European flints are all coming from surely reactive areas. All the samples collected in situ are of dense flint, surrounded by a less or more large zone of cortex (or porous flint); the color is very variable from gray to black, red or green, due to the presence of small amounts of impurities (the dust being always white). The beach samples are very similar to the previous ones, except for the often reduced presence of cortex (due to its easier erodibility).

The list of all the samples examined, with the name of the village nearest to the sampling zone, the color of the flint sample, the kind of the mother rock and the age of the formation, is shown in Tab.1.

Table 1 Location, description and age of the samples studied

Sample	Sampling zone	Flint color, mother rock	Age
IT 1, IT 11	Fossombrone (Marche)	Red, limestone	Paleocene
IT 2, IT 12	Pergola (Marche)	Gray, limestone	Lower Cretaceous
IT 3, IT 13	Gubbio (Umbria)	Red, limestone	Upper Cretaceous
IT 4, IT 14	Scheggia (Umbria)	Black, limestone	Upper Cretaceous
IT 5, IT 15	Ponte Calcara (Umbria)	Green, limestone	Upper Jurassic
IT 6, IT 16	Corno di Catria (Marche)	Gray-pink, limestone	Lower Cretaceous
IT 7, IT 17	Passo Capannelle (Abruzzo)	Pink, limestone	Upper Jurassic
IT 8, IT 18	Muccia (Marche)	Red, limestone	Lower Miocene
IT 9, IT 19	Tocco (Abruzzo)	Black, limestone	Jurassic
IT 10, IT 20	Introdacqua (Abruzzo)	Black, river pebbles	Jurassic
GB 1	Lyme Regis (England)	Gray, limestone	Lower Cretaceous
GB 2	Deal (England)	Gray, beach pebbles	Cretaceous
GB 3	Deal (England)	Red, beach pebbles	Cretaceous
GB 4	Salisbury (England)	Black, limestone	Upper Cretaceous
NL 1	Bruinisse (Netherland)	Gray, beach pebbles	Cretaceous
NL 2	Kappeln (Germany)	Gray, beach pebbles	Cretaceous
NL 3	Husum (Germany)	Gray, beach pebbles	Cretaceous
NL 4	Abenra (Denmark)	Gray, beach pebbles	Cretaceous
NL 5	Romo (Denmark)	Gray, beach pebbles	Cretaceous
NL 6	Bjerregard (Denmark)	Gray, beach pebbles	Cretaceous
NL 7	Zoutkamp (Netherland)	Gray, beach pebbles	Cretaceous

ANALYSIS: METHODOLOGIES AND RESULTS

The analysis of the specimens was carried out by mean of optical methods (petrographic examination of thin sections), chemical methods (kinetic test, ASTM C 289), physical methods (microhardness) and X- ray diffraction methods.

Optical methods

For each sample at least two thin sections, cut following the two main development planes of the samples, were examined, operating in polarized light (crossed and parallel nicols) with magnifications varying from 30x to 200x..

Each sample examined showed obviously some peculiar characteristics, but it was not possible to find, by this way, any feature tipically distinguishing the flints of different ages, whether Italian or north-European. It must be noted, however, that north-European flints typically show a very small cryptocrystalline quartz structure or

considerable amounts of chalcedony or both. The independence of the optical characters from the age clearly appears in the following Tab.2.

Table 2 Results of the petrographic examinations

Sample	Age	Quartz		Chalcedony	Porosity		Notes
		Cripto	Micro		Calcite	Empty	
IT 1, IT 11	Paleocene	---					
IT 2, IT 12	L.Cretac.	--			+++		
IT 3, IT 13	U.Cretac.	--		+			Fe hydrox
IT 4, IT 14	U.Cretac.	--	+	++	+	++	
IT 5, IT 15	U.Jurassic	--		+			
IT 6, IT 16	L.Cretac.	---		+++			Microfossil.
IT 7, IT 17	U.Jurassic	---			+++		
IT 8, IT 18	L:Miocene	--	+	+++	+++		UEQ (30°)
IT 9, IT 19	Jurassic	--	++	++			
IT 10, IT 20	Jurassic	--			++		
GB 1	L.Cretac.	--	+	++		+++	
GB 2	Cretac.	---	+	++			
GB 3	Cretac.	--	+	++			
GB 4	U.Cretac.	---	+	++	+		Microfossil.
NL 1	Cretac.	---		++			
NL 2	Cretac.	---		++			
NL 3	Cretac.	--	+	++			
NL 4	Cretac.	---		+++			
NL 5	Cretac.	---		++			
NL 6	Cretac.	---		++			
NL 7	Cretac.	---		+++			

Cryptocrystals dimension: - small, -- very small; --- very very small
Relative abundance: + scarce; ++ medium; +++ high
UEQ ( ): undulatory extinction quartz and related extinction angle

Chemical methods

The ASTM C 289 method

The tests were carried out following this method: a 25-g sample crushed to 0.30 to 0.15 mm and treated with a 1N solution of NaOH at 80 °C for 24 hours, analysis of reduction in alkalinity and dissolved silica on the filtrate.

Only about one half of the samples was tested by this method, that already gave unsatisfactory results for the Italian aggregates (Barisone & Restivo 1992a); these determinations were made only in order to make a comparison among the dissolution speed of silica in the different flints tested.

It must be noted, however, that no clear correspondence appears among these data and the age or the petrographic examination results. The data obtained by this test are shown in Tab.3, together with those obtained by the kinetic test.

The kinetic test

The tests were carried out following the outlines given by the conceivers of this method (Sorrentino et al. 1991, Sorrentino et al 1992): a 25-g sample crushed to 0.30 to 0.00 mm (smaller than 0.100.mm about 40 %), treated with 25 ml of a 1N solution of NaOH at 80 °C for 72 hours, analysis of SiO_2/Na_2O ratio on the filtrate after 24, 48 and 72 hours.

All the samples were so tested, mainly in order to obtain further data on the dissolution speed of silex, taking into particular account the SiO_2 content of the solution after 72 hours; nevertheless, also the Na_2O content was measured.

The results obtained after 72 hours are synthesized in the following Tab.3, together with those obtained by the ASTM C 289 test. As it can be seen, there is no clear separation between the SiO_2 or SiO_2/Na_2O values obtained for north-European or Italian flints; moreover, the trend shown by these data is not in accordance with those shown by the ASTM C 289 method or the petrographic examination.

Table 3 ASTM C 289 and kinetic test final results

Sample	ASTM C 289 test		Kinetic test (72 hours)		
	Rc (mmol/l)	Sc	Na_2O (mmol/l)	SiO_2	SiO_2/Na_2O
IT 1, IT 11	215	547	259	2050	7.91
IT 2, IT 12			238	1500	6.30
IT 3, IT 13	183	362	251	1580	6.29
IT 4, IT 14			241	1167	4.84
IT 5, IT 15			335	1830	5.46
IT 6, IT 16	139	451	484	2660	5.49
IT 7, IT 17			359	2230	6.21
IT 8, IT 18	277	346	287	1862	6.49
IT 9, IT 19	205	684	329	2453	7.45
IT 10, IT 20	195	128	196	1047	5.34
GB 1	115	728	328	1428	4.35
GB 2			234	1473	6.29
GB 3	173	681	286	1454	5.08
GB 4			306	1480	4.84
NL 1	115	732	285	1966	6.90
NL 2			268	1326	4.95
NL 3			294	1627	5.53
NL 4	206	752	267	2020	7.56
NL 5			312	2063	6.61
NL 6			298	1985	6.66
NL 7	162	646	243	1725	7.10

Physical methods

In order to evaluate the differences - on a small scale - among the flints analyzed, the microhardness on polished sections (approximatively 2 mm wide and 3 mm long) was measured. After a first phase, in which loads of 100g and 200g and steps of 1mm and 0.5 mm were used, all the determinations were executed with a 200-g load and a 0.5-mm step, in order to obtain a better precision and accuracy of the results.

It seemed logical to foresee higher values for the microhardness of the more crystalline flints; on the contrary, all the north-European flints, with a very small crystallization degree and significant amounts of chalcedony or of empty spaces or both, showed an average microhardness higher than 8 Gpa; the same result was obtained by only three Italian flints, without connection of age among them but all characterized by a relatively high chalcedony content or a high porosity (see Tab.2).

The data obtained by the microhardness tests are summarized in the Tab.4.

Table 4 Microhardness of the tested flints

Sample	Microhardness (Gpa)			Sample	Microhardness (GPa)		
	Min.	Aver.	Max.		Min.	Aver.	Max.
IT 1, IT 11	4.7	6.1	7.7	GB 1	6.1	8.2	10.3
IT 2, IT 12	2.4	6.7	9.6	GB 2	7.7	8.9	9.9
IT 3, IT 13	6.1	7.9	9.4	GB 3	6.3	8.1	9.2
IT 4, IT 14	7.3	8.7	9.9	GB 4	7.5	9.1	10.2
IT 5, IT 15	5.6	6.8	7.7	NL 1	7.1	8.6	10.5
IT 6, IT 16	7.5	8.4	9.6	NL 2	7.3	8.5	10.2
IT 7, IT 17	5.8	7.4	9.1	NL 3	6.8	8.2	9.7
IT 8, IT 18	7.2	8.2	9.9	NL 4	6.2	8.3	9.6
IT 9, IT 19	7.2	7.4	8.6	NL 5	7.1	8.7	9.8
IT 10, IT 20	6.8	7.6	9.5	NL 6	7.0	8.2	9.2
				NL 7	6.9	8.4	10.0

X-ray methods

This analysis method is usually adopted for identification of crystalline materials, being based on the diffraction of X-rays caused by the crystalline structure, and it is usually considered unsuited for poorly crystallized materials, such as flints. However, the peculiar purposes of this research, aiming simply to detect the differences in the degree of crystallization, led to suppose an useful employment of this technique.

The analyses were carried out on all the samples, operating with the following parameters: CuKα radiation, 40 kV, 30 mA, scan speed 5, sampling interval 0.05, investigation interval 3° to 50° (2θ). The samples were crushed to pass 0.04 mm, and the dusts so obtained pressed in the samples containers without additives, in order to obtain the maximum density.

The spectra so obtained showed the dominating presence of quartz, with occasionally subordinate calcite; in order to verify possible differences in low diffracting minerals content (opal, chalcedony, etc.), an amplification of the 3°-15° (2θ) intervals was made. In Fig. 2 some examples of these diffraction diagrams can be seen; all the north-European flints are characterized by the presence of a secondary peak at 2θ = 6°-6.2° (silicon oxide hydrate), peak that nevertheless appears also in some Italian samples (IT 4, IT 5, IT 6, IT 7).

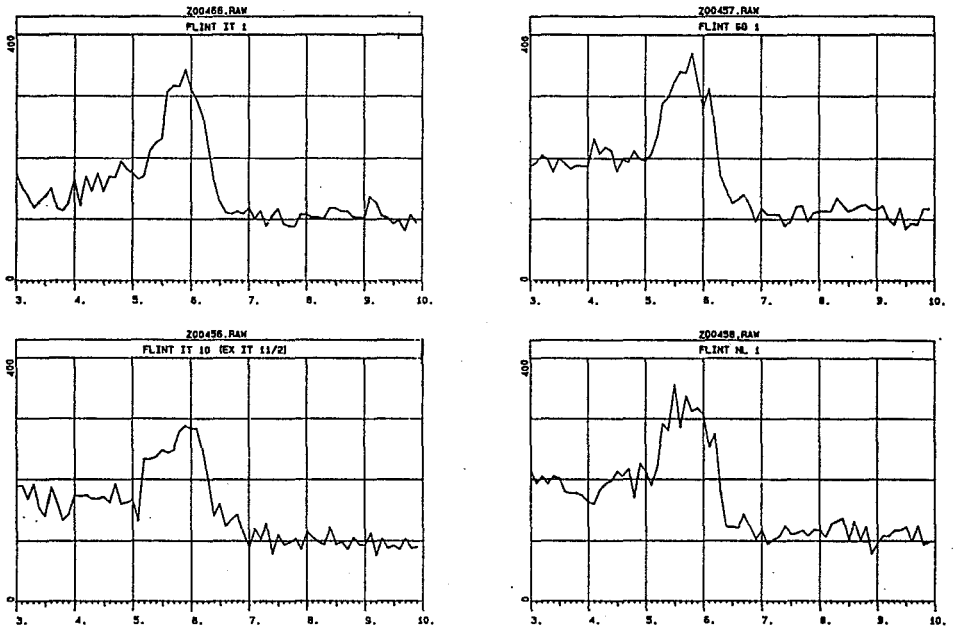

Fig.2 Diffraction diagrams, in the interval 3°-10°, of some flint samples (IT 1 and IT 10 at left, GB 1 and NL 1 at right)

CONCLUSIONS

The results obtained by the analysis carried out, results not agreeing at all, reject the existence of a correlation between the geological age and the reactivity of the flints examined.

At the present stage of the study, it is possible that the normally higher reactivity of north-European flints in relation to the Italian ones is linked to a structural disorder at electron microscope scale or, more probably, to an higher porosity mainly due to the different weathering conditions suffered by the flint fragments during their transportation and staying in alluvial deposits.

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REFERENCES

Andersen, K.T. & Thaulow, N. 1990, 'The application of undulatory extinction angle (UEA) as an indicator of alkali-silica reactivity of quartz', RILEM internal report.

Barisone, G. 1984, 'Petrographic analysis of aggregates related to alkali-silica reaction', Proc. Symp. Int. sur les granulats, Nice, Bull. I.A.E.G., 30, pp.177-181.

Barisone, G. & Bottino, G. & Cardu, M. 1986, 'Italian peninsular aggregates and the alkali-silica reaction', Proc. V Int. Congr. of I.A.E.G., Buenos Aires, pp.1623-1632.

Barisone, G. & Restivo, G. 1992a, 'Alkali-silica reactivity of alluvial deposits evaluated using chemical and psammographic methods', Proc. IX Int. Conf. on Alkali-aggregate reaction in concrete, London, pp.46-52.

Barisone, G. Restivo, G. 1992b, 'Alkali-silica potential reactivity of undulatory extinction quartz in the Western alpine arch', Proc. IX Int. Conf. on Alkali-aggregate reaction in concrete, London, pp.40-45.

Baronio, G. 1984, 'Granulats reactifs aux alcalis utilises en Italie', Proc. Symp. Int. sur les granulats, Nice, Bull. I.A.E.G., 30, pp.183-186.

Christensen, P. & Chatterji, S. & Thaulow, N. & Jensen, A.D. 1983, 'Alkali-silica reactivity of various danish flint types', Proc. VI Int. Conf. on Alkalies in concrete, Copenhagen, pp.315-319.

Lenzner, D. & Ludwig, U. 1978, 'Alkali-aggregate reaction with opaline sandstone from Schleswig-Holstein', Proc. IV Int. Conf. on Effect of alkalies in cement and concrete, Purdue, pp.11-35.

Palmer, D. 1981, 'Alkali-aggregate reaction in Great Britain - The present position', Concrete, V, 3.

Rayment, P.L. 1992, 'The relationship between flint microstructure and alkali-silica reactivity', Proc. IX Int. Conf. on Alkali-aggregate reaction in concrete, London, pp.843-850.

Rossetti, V.A. & Chiocchio, G. & Sciotti, M. & Peroni, G. 1988, 'Indagine sulla reattivita` degli aggregati dell'Appennino orientale', Autostrade, 30, 2.

Sorrentino, D. & Sabio, S. & Junique, D. 1991, 'Attaque alcaline des granulats: mise au point d'un test cinétique', Annales ITBTP, 499, Série Essais et mesures, 235.

Sorrentino, D. & Clement, J.Y. & Golberg, J.M. 1992, 'A new approach to characterize the chemical reactivity of the aggregate', Proc. IX Int. Conf. on Alkali-aggregate reaction in concrete, London, pp.1009-1016.