

THE CHARACTERIZATION OF POTENTIALLY REACTIVE AGGREGATES

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All rocks are considered to be possibly reactive. Those materials exhibiting significant levels of reaction at realistic alkali levels are characterized by the presence of a small percentage of silica minerals in particles of less than 5 micrometres in a structure which is either porous or contains other flaws such as fine cracking or microcracking developed by geological factors or in manufacture. The undulose extinction of quartz is regarded as less significant than the presence of strain lamellae or a cryptocrystalline porous fabric.

INTRODUCTION

The concept of specifying aggregates that might be used safely and those that should be avoided has undeniable attractions. The alternative is that all aggregates should be tested on a regular basis and perhaps that some certification of quality should be provided by the supplier. Both approaches require a reliable assessment of whether or not potentially reactive components are present. In the United Kingdom, lists have been compiled for the purpose of both diagnosing the presence of reaction in existing structures and for specifying to avoid the reaction in new construction. The lists include rock types that are judged to be innocuous in local experience, with alternative lists giving materials that are considered potentially reactive. Avoidance of opal, cristobalite, tridymite, and metaquartzite is specified. chert and microcrystalline silica should be less than 2% (or perhaps more than 65%). Other rocks or minerals considered to be potentially reactive include chalcedony, chalk (because of the possible presence of flint), chert, diorite, microdiorite, greywacke, opaline silica, microcrystalline, cryptocrystalline or strained quartz, quartzite as a sedimentary or metamorphic rock, some sandstones, rhyolite and volcanic glass. This list includes materials that have not necessarily led to the production of serious or even moderate deterioration and it is recognised that other rocks may have exhibited reaction in other countries.

Rocks that have not been found to be reactive in the United Kingdom are presumably all the rest. The following are mentioned: limestone, dolomite, arkose, breccia, conglomerate, gritstone, slate, schist, amphibolite, gneiss, granulite, marble,

hornfels, tuff, trachyte, basalt, dolerite, gabbro, andesite, syenite, microsyenite, granite and microgranite. The author has found examples of limestone, slate, and granite that have produced some reaction and one of the most damaged concretes is dominated by reactive argillite. The lists of both reactive and unreactive rocks therefore require continuous modification and must be treated with caution. They do not provide guarantees that particular rocks are safe or unsafe and many rocks are not even on the lists.

Mather (1), considers that all aggregates are reactive; they differ only in the kinds of reaction and the degree and rate to which the reaction proceeds and in its effects. Worldwide experience provides a long list of rocks that have been considered to have produced significant levels of reaction (Table 1), all of which probably contain either a silica mineral or glass.

TABLE 1 - Some of the rocks found to be reactive

<u>Sedimentary rocks</u>	<u>Igneous rocks</u>	<u>Metamorphic rocks</u>
orthoquartzite	andesite	quartzite
shale	rhyolite	phyllite
greywacke	rhyolitic tuff	granite gneiss
sub-greywacke	silicified tuff	slate
chert	devitrified glass	amphibole
siliceous limestone	granite	metabasalt
siliceous dolostone	pumice	hornblende schist
sandstone	tuff	metadolerite
argillite	dacitic tuff	mica schist
arkose	diorite	
taconite	dacite	
chalcedony	dacitic tuff	
opal	obsidian	
marl	trachyte	
	felsite	
	basalt	
	gabbro	
	granophyre	

In addition to the widely recognised problems associated with the presence of opal, chalcedony, cristobalite, tridymite, and chert, early diagnoses of the reaction recognised the reactivity of andesite and rhyolite and related materials such as obsidian, trachyte, dacite, tuff, and felsite. These names have since recurred repeatedly in the literature. Volcanic and artificial glasses can clearly be very reactive wherever they can occur as can greywackes and related rocks such as quartzwackes, argillites and siltstones, quartzites and metaquartzites and phyllites.

The list of reactive rocks shows that Mathers' statement ought to be regarded as the starting point for the assessment of potential for the reaction. Dolan-Mantuani (2) pointed out the converse truth - that acceptance of general descriptions of reactive rocks leads to unnecessary testing of rocks which could and ought to be

identified as innocuous. There is clearly a need to specify more precisely the characteristics of rocks that are likely to lead to damaging reaction.

GEOLOGICAL ASSOCIATIONS

Geological maps show that the materials found to be reactive represent the main lithologies of most regions of the crust. Former sites of continental collision, might provide argillite, greywacke-type sandstone, sequences of intermediate and acidic volcanics, pyroclastics, and both basic and acidic intrusives that are all liable to have been deformed, sheared, recrystallized, hydrothermally altered, and veined, both by sulphides and silicates. Quarried rocks and worked sands and gravels in such areas are considered suspect. Indeed, where the rocks can be worked for metallic minerals, they may present the highest risk when they or their gravel and sand derivatives are to be used as aggregates. In other regions where for example the ophiolite assemblage is encountered, hydrothermal alteration is also likely and bedded and reworked cherts are widespread. Consideration must also be given to the changes occurring in the rocks during the formation of sands and gravels. Cherts because of their intrinsic resistance to abrasion, can become dominant in sands and gravels but are also changed in the make-up of the deposits. Flint in gravel, for example, differs substantially from that found in the original Cretaceous nodule. Each geological source will possess characteristics pointing to possibly deleterious materials in potential aggregates. The sequences of Caledonian metaquartzites, metagreywackes and argillites of Scandinavia extend through Scotland and Ireland and into North America. The Ordovician reactive dolomite limestones of Canada run through the Eastern USA and the Steinman trinity can be recognised in most former orogenic belts.

AMOUNT OF REACTIVE COMPONENT

The substances taking part in reaction are always a very small fraction of the rock. Even where cracking is severe, consideration of the normal volume proportion of gel makes it doubtful that more than about 1% of the silica in the rocks has been converted into gel. This would represent consumption of some 17 kg/m³ of silica and 5 or 6 kg/m³ of alkali. The gel outside the aggregate usually has much less alkali than that in the aggregate, but there is also usually remnant alkali in the surrounding cement paste. There can be little doubt that alkali concentrations are in fact maintained in the paste at a moderate level throughout the reaction. Hence, consideration of alkali levels in the gel and in the remaining paste show that the total silica consumption must always be a very small fraction of the total mass of the aggregate. This makes it particularly difficult to identify reactive components.

AVAILABILITY OF REACTIVE SILICA

Reactions normally take place inside the aggregate and the reactive silica must be accessible to both the alkalies and to

moisture. Even in mortar bars and concrete containing silica glass, the gel occurs in cracks within the aggregate and gel production and crack generation take place within the aggregate.

The form of the fine cracking generated by the reaction depends on the nature of the reactive aggregate and its size range. In samples containing cherts for example, the size of the cracks varies with the size of the chert particles. Cherts of less than a millimetre in mean dimension produce extremely fine cracks that penetrate into the paste for only a few micrometres. The cracking and consequent expansion generated by larger reactive cherts, perhaps 5 or 6 mm in mean dimension, is much greater and the cracks within these cherts frequently extend from one chert to another and may run for some tens of centimetres through the concrete. Other rock types such as greywacke and argillite and some metaquartzites tend to show the relationship that the cracking is most obvious and severe where the reaction occurs in the larger rock fragments. It is also common to find that an increasing amount of damage occurs as the amount of the larger reactive rock fragments increases.

The accessibility of the reactive components to the pore fluid must be governed by the structure of the rock. There is evidence that the outer parts of some cherts have smaller capillary pores than the central parts where ribbons of highly reactive silica may occur within the larger pores. The small pores may effectively pump alkaline solutions into the cherts. In concretes taken from indoors, it has been found that the inner parts of such cherts are highly alkaline and may contain needles with exceptionally high alkalis (e.g. greater than 70% by weight of K_2O) when they are dried out and where little or no gel has been formed.

Aggregates such as argillite, greywacke, or metaquartzite typically show the main cracking in the larger aggregate pieces. In one example of greywacke more than 150 mm across, a single crack was found to pass through the rock and to have some 2 mm thickness of soft fluid gel. There is little or no difference between the rock along the cracks and that occurring elsewhere in the aggregate particle and if mortar bars are made of the unreacted material, this is also found to be reactive. The location of the reaction therefore relates to the accessibility of the reactive material to the alkalis and this may occur through the presence of planes of weakness generated in the crushing or through a natural fracture, possibly occurring along a bedding plane or cleavage. In some metaquartzites the cracks containing gel run along thin zones made of finely divided and possibly cataclased quartz where a plane of weakness was certainly present in the original rocks.

STRUCTURE OF REACTIVE ROCKS

The reactive parts of rocks typically contain finely divided silicate minerals generating a high total surface area. This must be a predominant factor in promoting the damaging reactivity. Midgley's data, (1951), (3) make the point: surface areas of 400,000 cm^2/g for opal, 4,300 cm^2/g for chalcedony,

2,200 cm²/g for microcrystalline flint down to about nothing for coarsely crystalline quartz. See also Gratten-Bellew (4)

Chert:

Various studies have been made of the structure of flint and other cherts Clayton (4). These show that the nature of chert varies with its origin and subsequent history. Chert mostly consists of quartz grains in spherical clusters of between 5 and 20 micrometres in diameter (lepispheres). These are variously packed together in structures which vary from very dense to open porous forms in which the spheres are hardly in contact. Between the spheres is a fibrous cement of microchalcedony containing incorporated water. This chalcedony may be recrystallized and makes the chert white. It is liable to ready solution. There is also a late stage quartz infilling of cavities which ranges from chalcedony to well formed quartz crystals. Other forms of chert may be largely composed of chalcedony in radiating bundles 1 to 5 mm in length with fibrous sheaths. (Hirche, 1975, (5), shows that high water and OH ions occur in such reactive aggregates.)

In many cherts, sponge spicules and other siliceous fossil remains occur which may be opaline. These are often converted into quartz having the form of chalcedony through geological time. Where the chert occurs in gravels, it has usually been variously weathered. It may become more porous and certainly changes its structure. Reactive cherts that the author has examined are composed of the microcrystalline aggregates of quartz forming roughly spherical structures which are linked by ribbons of secondary silica which seems to be amorphous. Another characteristic of damaged reactive cherts is that they are often pebbles with a zonal structure parallel to the surface of the pebble. The zones exhibit different particle sizes and different degrees of porosity. It is quite common in thin section to find that these cherts appear white in reflected light but brown when seen in transmitted light. This characteristic is a feature of cherts that contain interstitial cryptocrystalline chalcedony with water in the structure. It is a feature that is almost always associated with some degree of reactivity. Poole, 1983 (6) has shown that the reactivity of flint also varies with the amount of silica present and that the higher the proportion of other components, the greater the potential for reaction. Brownish cherts, as seen in reflected light, tend to be more reactive than dark grey to black cherts. This largely relates to the porosity of the material and hence to its density and chert particles having a bulk density of less than 2.50 are at risk.

Argillites and greywackes:

Gratten-Bellew (8) showed that an argillite having high expansion had more than 80% of microcrystalline particles. Electron microscope photographs show the presence of abundant grains only a few micrometres in maximum dimension. Similar reactive argillite from Northern England has particles of only a few micrometres in diameter in thin layers and in this rock several cracks containing gel only a few micrometres thick run along the layering. Reactive greywackes also have a very fine grained

matrix with quartz, feldspar, epidote, and chlorite occurring as grains less than 10 micrometres.

The list of these types of reactive rock is characterized by the presence of such microcrystalline material. Evidence from metals shows that the transport of ions through solids is roughly in the order transport through pore fluid is very much more rapid than transport along grain boundaries, which is very much more rapid than transport through the solid. Reaction rates are likely to be governed by the transport of alkali and hydroxyl ions in pore fluids and along grain boundaries and not through the main mass of most rocks. Those rocks belonging to the late slow expanding category tend to have low water absorption and microporosity relative to the more usual rapidly reacting materials. The slower reaction rate may therefore relate to the process of reactant transport along fine cracks or grain boundaries. Penetration of moisture is evidently required for the reaction to be expansive and reactive rocks must be characterized by a high potential surface area for the silicates and access to this high surface area for the pore fluid.

Reactive quartzites:

Rocks containing strained quartz have often been recognised as reactive and recipes for the measurement of strain such as that given by Dolar-Mantuani, 1983 (9) have been used to indicate the potential for reaction. However, if it is accepted that the amount of material actually taking part in a reaction is about 1% of the total aggregate, there is little point in measuring the total amount of strained quartz. The method of measurement is also subject to serious errors, (Anderson and Thaulow (10), Grattan Bellew 1988 (11)), and in the author's view does not indicate the degree of strain present in the quartz. Several hundred strained quartzes have been measured in diverse rocks and these show that the value obtained for the undulose extinction angle is dependent on the recognition of the strain domains boundaries in the quartz. If an individual domain of strain is carefully identified, it is found that the undulose extinction angle rarely exceeds 4° . The measurement of values in excess of 4° usually relates to extinction passing through several strain domains and larger quartzes often show higher overall undulose extinction angles. Sometimes a position may be found in which the direction of rotation of the undulosity becomes reversed in a single grain.

Where quartzes are strained, the effect is to produce a number of features. These are as follows (Vernon 1976, (12))

Extinction bands (undulose extinction): These are bands which are roughly elongate sub-parallel with the 0001 crystallographic plane and which are formed by bending of the lattice in response to slip on the 0001 plane. It is inconceivable that single domains of quartz can sustain such deformation that the true undulose extinction angle is much in excess of a few degrees without a grain boundary being formed.

Deformation bands: These are similar to extinction bands, but vary considerably in orientation, though many lie sub-parallel with or nearly normal to 0001 and are formed by slip on the 0001 plane accompanied by bending of the slip planes. They are optically very similar to extinction bands and might be confused with undulose extinctions.

Deformation lamellae: These are narrow planar or lenticular structures which have various orientations. Often two or more orientations occur in the same space. They terminate inside grain boundaries and are often normal to the undulose extinction bands. Hence they are most often visible in the quartz grains that are cut at right angles to the C crystallographic axis. Their orientation is variable and is dependent on the type of deformation. Common orientations are at an angle of between 5 and 30° to 0001 or almost at right angles to 0001. The latter are very common for example in deformed quartzites from the Caledonian of Sweden. Truly basal lamellae occur only in impact metamorphosed rocks where the strain rates are exceptionally high. The strain lamellae are best seen in sections that are slightly thicker than normal and are difficult to find in thin sections of less than 30 micrometres. They are a micrometre or two in thickness but can be followed for tens of micrometres along their lengths. It is not uncommon to find two sets of strain lamellae developed oblique to one another. They sometimes resemble the characteristic crossed hatched twin structure of microcline. These structures must represent a change in crystal structure on a very small scale that is almost certainly dependent on movements along lattice dislocations. It is the author's experience that wherever metaquartzites or rocks containing strained quartz are reactive, the quartz grains exhibit either strain lamellae or are cataclased or otherwise contain microcrystalline to cryptocrystalline grains on larger grain boundaries or along fracture planes of various types. Transmission electron microscope studies have shown that the reactive material in some greywackes is quartz exhibiting a large number of dislocations. The nature of the reaction in the quartzites and greywackes is probably much the same.

Reactive limestones:

The reactive component of siliceous limestones is generally virtually indecipherable with the optical microscope. The particles tend to make the limestone dark and may form argillite-like layers. The reactive material is generally dispersed through the limestone and the mode of cracking closely resembles that found for quartzites and greywackes. This reactive material often occurs in bituminous limestones where dark patches are composed of clay-grade material blended with traces of bitumen. The bitumen in these rocks is almost unaffected by organic solvents but is readily moved by strongly alkaline solutions so that the pore fluid is attracted to the bitumen and is capable of moving the bituminous material into the surrounding paste. The silicate materials include illite and quartz and the particle size of this material is typically less than 5 micrometres.

Amorphous material:

In some cases the reactive material is sufficiently fine for it to be at least optically amorphous. This includes some glasses and devitrified glasses. Many volcanic rocks that appear glassy in thin section are in practice crystalline when seen with the electron microscope but have particle sizes of less than a micrometre or two. Where the crystallinity is less than that of fully developed alpha quartz, the material sometimes produces poorly defined X-ray diffraction lines and this has been used to define a crystallinity index (e.g. Morino 1989 (14)). It is not always easy to identify the presence of such material since a search is being made for what might be one or two percent of the rock, and it is unlikely that such very fine grained or amorphous material will be detected by the X-ray procedure.

CONCLUSIONS

It is concluded that rather than identifying specific rock types as characteristically reactive and others as unreactive, a survey of rock types under consideration should be carried out with a view to establishing the following features:

- (i) Is the material microporous, either locally or in total?
- (ii) Does the rock contain fractures or protofractures or thin layers which will provide an access for the alkaline pore solutions?
- (iii) Are there materials present which have particle sizes of 5 micrometres or less and which almost certainly include silica minerals or siliceous glass.
- (iv) Are there particles in accessible parts of the aggregate which have dislocations in quartz, as shown either by electron microscopy or by optical examination for the presence of strain lamellae (not undulose zones, though there is sometimes an association of thin lenticles of undulose quartz with quartz containing strain lamellae)?
- (v) Is there evidence of the presence of the specifically reactive phases such as chalcedony, opal, or related materials, perhaps seen through the presence of water in the structure making for particular colours or identified by X-ray procedures?
- (vi) Does the X-ray diffractogram indicate the presence of amorphous or exceptionally fine material?
- (vii) Are traces of gel produced when particles over 0.5 mm in diameter are treated with molar NaOH/KOH solution.

If materials having appropriate combinations of these characteristics are present, then the rock should be regarded as potentially reactive. On a first examination this potential for reaction may be suspected simply from the observation that the

particle size in some zones is too fine for the particles to be resolved with a high quality petrological microscope.

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