Industrial Minerals Laboratory Manual

LIMESTONE

D J Harrison
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Cover illustration:
Acetate peel of a stained bioclastic dolomitic limestone. Coarse fragments of crinoid, coral and brachiopod lie in a fine spar matrix. Pink/purple areas are composed of calcite or ferroan calcite; turquoise areas are ferroan dolomite.

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Keyworth, Nottingham, British Geological Survey, 1993
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Preface

Industrial mineral raw materials are essential for economic development. Infrastructure improvement and growth of the manufacturing sector requires a reliable supply of good quality construction minerals and a wide range of other industrial mineral raw materials.

Although many less developed countries have significant potential industrial mineral resources, some continue to import these materials to supply their industries. Indigenous resources may not be exploited (or are exploited ineffectively) because they do not meet industrial specifications, and facilities and expertise to carry out the necessary evaluation and testwork are unavailable. Unlike metallic and energy minerals, the suitability of industrial minerals generally depends on physical behaviour, as well as on chemical and mineralogical properties. Laboratory evaluation often involves determination of a wide range of inter-related properties and must be carried out with knowledge of the requirements of consuming industries. Evaluation may also include investigation of likely processing required to enable the commodity to meet industry specifications.

Over the last 10 years, funding from the Overseas Development Administration has enabled the British Geological Survey to provide assistance to less developed countries in the evaluation of their industrial mineral resources. This series of laboratory manuals sets out experience gained during this period. The manuals are intended to be practical bench-top guides for use by organisations such as Geological Surveys and Mines Departments and are not exhaustive in their coverage of every test and specification. The following manuals have been published to date:

- Limestone
- Flake Graphite
- Diatomite
- Kaolin
- Bentonite

A complementary series of Exploration Guides is also being produced. These are intended to provide ideas and advice for geoscientists involved in the identification and field evaluation of industrial minerals in the developing world. The following guide has been published to date:

Biogenic Sedimentary Rocks

A J Bloodworth  
*Series Editor*

D J Morgan  
*Project Manager*
Limestone

1. INTRODUCTION

Limestone and other carbonate rocks are extremely valuable raw materials and are widely used throughout industry, although the construction and cement manufacturing industries are generally the principal consumers.

Strategic evaluations of national or regional limestone resources or site-specific reserve estimations need to involve far more than a basic geological appraisal and should include laboratory determinations of physical, mechanical, chemical and mineralogical properties of the stone. The evaluation also needs to include a comparison with national or international specifications for each potential end use.

This manual outlines the major industrial uses of carbonate rocks and describes the preferred laboratory procedures for evaluating their specific properties.

This manual is one of a series produced as part of the BGS/ODA R&D Project 'Minerals for Development'.
2. GEOLOGICAL OCCURRENCE

2.1 Sedimentary carbonate rocks

The geological classification of carbonate rocks is based on mode of occurrence and mineralogy. Limestone is a sedimentary rock composed mainly of calcium carbonate (CaCO₃), occurring as calcite or occasionally aragonite in recent deposits. Dolomite is a similar sedimentary rock in which dolomite (CaMg(CO₃)₂) predominates. Most dolomite is formed by the early replacement of limestone through the action of magnesium-rich waters. Around 20% of all sedimentary rocks are limestone or dolomite or gradations between the two. Common impurities in sedimentary carbonate rocks include clay minerals, silica (clastic material and/or chert), organic matter and iron oxyhydroxide minerals.

Most carbonate sediments have been produced by biogenic processes and consist of the skeletons of carbonate-secreting organisms, although some have formed as a result of inorganic chemical precipitation. Organic carbonates comprise the whole skeletons and fragments of larger organisms including corals, bryozoans and molluscs, as well as calcified parts of simpler organisms such as foraminifera and algae. In the geological record there are examples of major carbonate systems in which each of these groups has been the dominant carbonate producer. Inorganic carbonates occur as grains (principally ooids) and/or pore-filling cement precipitated directly from sea water. Cements generally represent a major contribution to carbonate reef sediments.

The size and purity of a carbonate deposit depend on its environment of deposition and subsequent diagenetic history. A minimal level of clastic input to the marine environment is required in order to accumulate relatively pure carbonate sediments.

Chalk is a very fine-grained micritic limestone, mostly consisting of the debris from planktonic algae. Chalk is the dominant carbonate in the Cretaceous of Europe and North America. It is usually white in colour and relatively soft and porous.

Other sedimentary carbonate rocks include marl, travertine and vein calcite. Marl is a general term for a limey mud or an intimate mixture of clay and limestone. Travertine is formed by rapid precipitation of calcium carbonate around hot springs. It is deposited in compact, fibrous or concentric layers producing a banded appearance. The softer and more porous form of travertine is known as calcareous tufa. Coarsely crystalline vein calcite is commonly associated with epigenetic baryte, fluorite and lead and zinc ores.
Limestone

2.1.1 Limestone classification

Limestones may be classified on the basis of grain type and grain size (Folk, 1959) or by their depositional texture (Dunham, 1962). The Folk system (Figure 1) describes the rock in terms of discrete grains (such as biogenic fragments) or 'allochems', dispersed to a greater or lesser extent in a matrix of microcrystalline calcite ooze ('micrite'), or a crystalline cement ('spar'). This classification is best applied in petrographic studies. The Dunham classification (Figure 2) is also widely used, particularly in the field description of carbonate rocks. This system subdivides rocks on the basis of their depositional texture; the presence or absence of fine-grained material differentiates a 'muddy carbonate' from a 'grainstone'. The relative abundance of grains allows muddy carbonates to be subdivided into 'mudstone', 'wackestone' and 'packstone', and the presence of signs of binding during deposition characterises 'boundstone'. The degree of packing differentiates 'packstone' from 'wackestone'. The former is composed of grains in close contact with each other whereas the latter consists of a relatively small amount of grains 'floating' in a mud matrix.

2.2 Igneous carbonate rocks

Carbonatites are an uncommon group of igneous rocks composed principally of calcium, magnesium and/or iron carbonates which generally occur as a component of intrusive alkaline ring complexes in areas of ancient basement or as intrusive or volcanic rocks within graben structures. Carbonatites are normally heterogeneous and may contain veins and xenoliths of other igneous rocks. However, they are often useful local sources of carbonates in areas otherwise devoid of limestones. Carbonatites may also host other economic minerals such as phosphates, vermiculite and rare earths.

2.3 Metamorphic carbonate rocks

Limestone or dolomite which has recrystallised during metamorphism is known as marble. Marble is an important source of carbonate rock, particularly in Archean shield areas. Mineral impurities include quartz, mica, chlorite, tremolite, actinolite, graphite, hematite and limonite. Pure marble is brilliant white but the presence of impurities results in texture and colour variations. The recrystallised fabric allows production of a polish on cut surfaces and this factor, together with its low porosity and its aesthetically pleasing appearance, results in wide usage as a dimension stone.
**Limestone**

<table>
<thead>
<tr>
<th>Volumetric allochem composition</th>
<th>&gt;25% intraclasts</th>
<th>&gt;25% oolites</th>
<th>&lt;25% oolites</th>
<th>Volume ratio of fossils: pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;25% intraclasts</td>
<td>Intrasparrite</td>
<td>Oosparrite</td>
<td>Biosparite</td>
<td>3:1 to 1:3</td>
</tr>
<tr>
<td>&lt;25% oolites</td>
<td></td>
<td></td>
<td>&lt; 1:3</td>
<td></td>
</tr>
<tr>
<td>&lt;25% oolites</td>
<td></td>
<td></td>
<td>&gt; 3:1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Depositional texture recognisable</th>
<th>Depositional texture not recognisable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original components not bound together during deposition</td>
<td>Original components bound together during deposition</td>
</tr>
<tr>
<td>Contains mud (clay and fine silt)</td>
<td>Lacks mud and is grain-supported</td>
</tr>
<tr>
<td>Mud-supported</td>
<td>Grain-supported</td>
</tr>
<tr>
<td>&lt;10% grains</td>
<td>&gt;10% grains</td>
</tr>
</tbody>
</table>

**Figure 1.** Classification of limestone (based on Folk, 1959).

**Figure 2.** Classification of carbonate rocks according to depositional texture (Dunham, 1962).
3. USES AND SPECIFICATIONS

The physical, mineralogical and chemical properties of carbonate rocks are widely utilised in many sectors of industry. Although the primary use of carbonate rocks is in construction, as aggregate or in the production of cement, they are also extensively used in the iron and steel industry, in the chemicals industry, in the manufacture of glass, and in many more specialised uses. In these non-constructional or 'high-purity' applications, limestone (or lime) may be used either as a chemically-reactive raw material or as an inert filler or pigment.

On heating (calcination) limestone forms lime (CaO) which is a 'basic' oxide and may be used to react with 'acidic' oxides (e.g. in the smelting process). Hydrated lime (Ca(OH)2) is formed by reacting lime with water (‘slaking’). Hydrated lime is an alkali which may be used for neutralising acidic solutions. Calcined dolomite is produced in a similar way and is commonly known as dolime.

Throughout the following text the term limestone includes dolomite, marble and chalk unless specifically excluded. The industrial functions of dolomite are generally, but not always, similar to those of limestone, although many industries use both minerals. For example, both limestone and dolomite are used in the manufacture of glass. Magnesium (required to inhibit devitrification) is provided by dolomite, with further addition of limestone to bring the calcium content of the glass to the required level.

A brief summary of the major end uses of limestone with an indication of typical specification requirements is given below and summarized in Figure 3. More detailed descriptions can be found in Harris (1982) and Department of the Environment (1991).

3.1 Construction uses

3.1.1 Roadstone

Harder limestones are commonly used in highway construction and in the UK, the USA and many other countries, roadstone is the largest single end use of limestone. Modern flexible road pavements consist of discrete layers. The 'sub-base' distributes the load onto the subsoil and is overlain by the 'roadbase' which is the main load-bearing layer. The surfacing layers consist of a 'basecourse' and a thin 'wearing course'. Limestone aggregates are most commonly used in the sub-base and roadbase layers where they are required to be clean and strong with low porosity.
Figure 3. Processing and major uses of limestone.
Limestones are typically less durable (they have a relatively low resistance to abrasion and a susceptibility to polishing) than many sandstone or igneous rock aggregates and hence are not generally used in road surfacing materials, which are required to be hard wearing and skid resistant. Specifications for materials used in road making in the UK are given in Department of the Environment (1976) and in relevant British Standards (BS 812, BS 882 etc.). Guidelines in the USA are provided by the American Society for Testing and Materials (ASTM). Other countries such as Germany and Australia have developed their own national standards for roadstone aggregates. There are no international standards (ISO) for aggregates, although draft European standards are in preparation by the Committee for European Standardisation (CEN). Some specification requirements for roadstone aggregates are given in Table 1.

### Table 1. Typical specification requirements for roadstone aggregates.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle density (specific gravity)</td>
<td>generally &gt; 2.65</td>
</tr>
<tr>
<td>Water absorption (an indicator of porosity)</td>
<td>&lt; 2%</td>
</tr>
<tr>
<td>Flakiness index (shape factor)</td>
<td>&lt; 25 (for wearing course)</td>
</tr>
<tr>
<td></td>
<td>&lt; 35 (for general purposes)</td>
</tr>
<tr>
<td>Aggregate crushing value (ACV strength test)</td>
<td>generally &lt; 24 or &lt; 30</td>
</tr>
<tr>
<td>Aggregate impact value (AIV strength test)</td>
<td>generally &lt; 25</td>
</tr>
<tr>
<td>10% fines value (strength test)</td>
<td>&gt; 160 KN</td>
</tr>
<tr>
<td>Aggregate abrasion value (AAV surface wear test)</td>
<td>&lt; 14 for lightly trafficked sights or &lt; 10 for potentially dangerous sites</td>
</tr>
<tr>
<td>Los Angeles abrasion value (LAAV attrition test)</td>
<td>&lt; 40 (for wearing course)</td>
</tr>
<tr>
<td></td>
<td>&lt; 50 (for base course)</td>
</tr>
<tr>
<td>Sulphate soundness test (disintegration by weathering test)</td>
<td>&lt; 18% magnesium sulphate loss</td>
</tr>
</tbody>
</table>

Note: This table shows specifications relating to typical British and American standards. Where test value limits are not specified, then guideline values are shown.

#### 3.1.2 Concrete aggregates

Concrete is usually made from a mixture of cement, coarse aggregate (gravel, crushed limestone or other hard rock) and fine aggregate (generally sand, occasionally finely crushed limestone). The properties of the aggregate affect concrete characteristics such as density, strength, durability, thermal conductivity, shrinkage and creep. The shape and
Limestone

Surface texture of the aggregate particles and their grading (distribution of particle sizes) are important factors influencing the workability and strength of concrete. Aggregates should not be of a type, nor contain sufficient impurities, that would have an adverse effect on the setting properties of the cement or on the durability properties of the concrete. They are therefore required to be hard, durable, clean and free of clay, shale, coal, organic material, pyrite or soluble sulphates and should not be subject to attack by an alkaline cement environment. The alkali-silica reaction (ASR) may induce expansion and cracking in concrete. ASR is a chemical reaction between disordered forms of silica, which may occur in aggregates, and hydroxyl ions formed by the release of alkali compounds from the cement. The reaction forms a swelling gel which may induce stress resulting in expansion and cracking.

A combination of the following may lead to ASR-induced cracking:

- A significant quantity of reactive silica (low reactive silica contents will not induce expansion);
- available alkalis (generally from the cement) above a critical level;
- water from an external source.

Reactive forms of silica (chert, quartz) can sometimes be present in limestone. There are a number of tests for assessing the reactivity of aggregates, such as the ASTM C289 quick test, the ASTM C227 mortar expansion test and the gel pat test (Jones and Tarleton, 1958). There are also guidelines for minimizing ASR in new constructions by using aggregates that contain less than 2% or more than 60% chert and flint (Concrete Society, 1987; Department of Transport, 1986). Any quartz in the aggregate should not be in the form of quartzite and should contain less than 30% highly strained quartz. More detailed summaries of ASR are given by Hobbs (1988) and the Concrete Society (1987).

Aggregates selected for use in concrete should comply with British Standard specifications (BS 882) or other national standards. When the use of materials not complying with such specifications is unavoidable, it should be demonstrated that sufficiently strong and durable concrete can be made with them.

3.1.3 Dimension stone

Hard limestones and marbles are popular building or ornamental stones. They are chiefly used as cladding to steel- or concrete-framed structures and as flooring material. Other than aesthetic appeal, the main requirement for limestone as dimension stone is its potential durability. The durability of a limestone is a function of its pore size. In particular,
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a stone with high microporosity is susceptible to the crystallisation of salts. Petrographic studies of limestones (Sedman and Barlow, 1989) have shown that several parameters, including cement type and grain size, directly affect building stone durability. Thus, fine micritic limestones are less durable than coarse spar-cemented limestones. Standard specifications for building stone are given in ASTM C568-89 (limestone) and ASTM C503-89 (marble). These standards, in conjunction with some UK Building Research Establishment (BRE) durability tests, are used extensively on an international basis for the selection of natural stone. However, physical properties of a building stone are generally of secondary consideration since aesthetic appeal (colour, texture) often predominate in the choice of stone.

3.1.4 Minor aggregate uses

A traditional market for limestone is railway ballast but the relatively low resistance of abrasion of most limestone aggregates when wet reduces the use of limestone in railway ballast in the UK. Igneous rock is usually preferred for this purpose. In other parts of the world limestone aggregates are widely used as railway ballast.

Substantial quantities of aggregate are used in land reclamation, site levelling and embankment construction. Specifications for such materials are generally undemanding and many of the softer and more porous limestones may be used. Limestone aggregates are also used for drainage materials in pipe bedding and filter drains. Large limestone blocks are used for sea defences and revetments in dams.

3.1.5 Cement

Cement is made by calcining a mixture of about 75% limestone and 25% clay to form a calcium silicate clinker which is then ground and mixed with a small amount of gypsum which acts as a setting retardant. Impurities in the raw materials which may affect the quality of cement include magnesium, fluorine, phosphorus, lead, zinc, alkalis and sulphides. Most national specifications for ordinary portland cement (OPC) require that the cement should not contain more than 6% MgO (less than 3% in the limestone); therefore the identification of dolomite is crucial in the assessment of carbonate rocks for cement manufacture. Other chemical specifications may limit SO$_3$ and P$_2$O$_5$ to less than 1% and total alkalis to less than 0.6%. Additional specifications may apply to speciality cement types, such as sulphate-resisting cement, oil-well cement and white cement (less than 0.01% Fe$_2$O$_3$).

The variety of raw material used worldwide for cement manufacture is very great. The blend of raw material can be adjusted to alter the
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chemical composition of the cement to the desired specification. Changes in the production process have allowed durable high magnesia cement to be manufactured (National Council for Cement and Building Materials, India, 1985). This process may allow the use of relatively high MgO limestones as cement raw materials.

3.1.6 Building materials

Lime is widely used in the building industry in the manufacture of calcium silicate bricks, lightweight concrete blocks, mortar, plaster and limewash. Calcium silicate bricks are manufactured from a mixture of lime and sand, together with pigments. The bricks are moulded to the same size as clay bricks and hardened in a steam press. Lime is also used in the production of aerated concrete blocks by the reaction of a slurry of lime and sand with powdered aluminium or zinc. This results in the production of hydrogen gas and a cellular structure within the cured block. Mortar is usually made from a mixture of cement, lime and sand. Lime is also used in cement-lime-sand plasters or as an additive to gypsum plasters. Limewashes, produced by adding water to lime or hydrated lime, are used for wall decoration and surface stabilisation.

3.2 Non-constructional uses: chemical

Limestone is used in a number of industries where chemical properties (basic oxide, neutralising agent, calcium content, flux etc.) are important. Most processes require lime or hydrated lime; only iron production, glass making and flue gas desulphurisation directly use raw limestone.

3.2.1 Iron and steel industry

Limestone or lime is used as a flux to assist melting in the extraction of iron from iron ore. The lime reacts with silica and alumina impurities in the ore and forms a slag which floats on the surface of the melt. High-purity limestone (or dolomite) with low sulphur and phosphorus contents are generally specified for this process, but consistency and local supply are usually the main criteria for acceptable materials.

Lime is also used as a flux in the steel industry and is required to remove silica and phosphorus from pig iron. Specifications for lime or calcined dolomite for steel flux demand high-purity material with low silica (less than 5% to 2%) and sulphur (less than 0.1%). Particle size, surface area and density of the lime are also important.
3.2.2 Soda ash manufacture

Sodium carbonate (soda ash) is an important raw material for the chemical industry and involves the reaction of carbon dioxide with a solution of brine and ammonia to produce ammonium chloride and a sodium bicarbonate precipitate. The precipitate is recovered and heated to produce sodium carbonate and the solution is treated with lime to release ammonia for recycling. The lime and carbon dioxide consumed in the process are obtained by calcining limestone, which should be of high purity (>98.5% CaCO₃).

3.2.3 Sugar refining

Limestone and lime are used in the sugar industry as part of the purification process. Lime and carbon dioxide (obtained by calcining the limestone) are used to adjust pH and to assist in precipitation of impurities. High-grade limestone containing at least 96% CaCO₃ and <1% SiO₂, <0.35% Al₂O₃ and <0.3% Fe₂O₃ is usually specified.

3.2.4 Glass manufacture

Most glass is made by fusing a mixture of silica sand, soda ash, limestone, dolomite and other materials. Limestone acts as a flux, allowing the mixture to melt at a relatively low temperature. Dolomite is added to inhibit the devitrification process through the addition of a small amount of magnesium to the glass. Stringent chemical specifications for limestone and dolomite used in glass making are usually specified. In particular, amounts of impurities which may colour the glass such as iron (varies from <0.05% to <0.02% depending on the type of glass), chromium, cobalt or nickel must be very low. Generally, very high purity limestones (>98.5% CaCO₃ or 55.2% CaO) are required for this application.

3.2.5 Flue gas desulphurisation (FGD)

Limestone is becoming widely used to reduce emissions of sulphur dioxide from gaseous combustion products in power generating plants. The limestone-gypsum process involves passing the flue gases through a circulating slurry of limestone and water. Sulphur dioxide dissolves and reacts with the limestone to form calcium sulphite which is then oxidised to gypsum. The gypsum may be a useful by-product. There are lower limits of quality required for the limestone, even for a 'throwaway' by-product. These are represented by a minimum CaCO₃ content of 90% and limitations on certain impurities. To ensure that FGD gypsum
saleable in US or European markets is obtained, high quality and consistent limestone feedstock is required. This should contain over 95% CaCO₃ and small amounts of SiO₂ (<0.65%), Al₂O₃ (<1%) and Fe₂O₃ (<0.25%).

3.2.6 Sea water magnesia

Hydrated lime (or slaked calcined dolomite) is used to precipitate the available magnesium in seawater as magnesium hydroxide. This is then calcined to give magnesia (MgO) which is used in the manufacture of refractories. A wide range of grades of magnesia is usually produced and the highest grade products require extremely pure raw materials for their manufacture. Typical specifications demand low SiO₂ (<0.15%), Al₂O₃ (<0.05%) and Fe₂O₃ (<0.15%).

3.2.7 Water purification and effluent treatment

Hydrated lime is used in the treatment of potable water to adjust the pH and to remove impurities. Lime is also used to condition sewage sludge and neutralise industrial effluents. Chemical and physical constraints on the type of limestone used to produce the lime are not usually specified.

3.3 Non-constructional uses: fillers and pigments

Limestone is relatively easily ground to a fine powder which is non-toxic, chemically inert and generally white in colour. These properties ensure that limestone powders are extensively used as fillers or pigments in a diverse range of industries. The primary purpose of a filler is to provide bulk to a product whilst saving on more costly raw materials. Some fillers also fulfill chemical functions, e.g. as a source of calcium in animal feeds and as an acidity regulator in pharmaceuticals and agriculture.

Many high-volume uses of limestone powders (including carpet backing, asphalt, coal mine dust) do not require pure limestone. Powders used in pharmaceuticals and food are required to be of very high purity and generally use precipitated calcium carbonate. Specifications for limestone powders used as fillers in paper, plastics and paints typically require closely controlled particle-size distribution and high brightness values, together with good rheological properties and low oil absorption. Typical brightness values for fillers for paper or plastic are 80 to 82%, values for paper coating typically range between 85 and 93% (ISO Standards).
Limestone powders are normally classified according to particle size range:

- **Coarse fillers** (generally low value); 75 µm to several millimetres, used for agricultural 'lime', animal feedstuffs, fertilisers, asphalt filler, mine dust.

- **Medium fillers** (generally medium value); less than 50 µm, used for carpet backing, floortiles, sealants, adhesives and putties.

- **Fine fillers** (generally medium value); maximum particle size 50 µm, 50% less than 2 µm, used for paper fillers, rubbers and plastics, cheaper paints.

- **Pigments and very fine fillers** (generally high value); maximum particle size 10 µm, 90% less than 2 µm, used in paper coatings, paints, rubbers and plastics.

Requirements for agricultural limestone are not very rigid. The main function is to reduce soil acidity, although it may also be used to increase levels of calcium or magnesium in the soil.
4. LABORATORY ASSESSMENT OF LIMESTONES

Evaluation of limestone deposits involves study of the geological setting and determination of the physical, mechanical, mineralogical and chemical properties of the stone. Limestone assessment should, therefore begin with an initial field investigation involving field mapping, section measuring and sampling. This will enable the general lithology to be described, as well as interpretation of stratigraphical relationships and geological structure. The main geological factors which need to be assessed at the field stage of investigations include:

- Presence of interbedded clays and other deleterious horizons (sandstones, igneous rocks etc.)
- Presence and distribution of clay-filled cavities
- Presence of chert and degree of silicification
- Presence and distribution of mineralisation (e.g., Cu, Pb, Zn ores, fluorite, baryte etc.)
- Degree and distribution of dolomitisation
- Staining by groundwater
- Structure of the deposit, structural discontinuities, degree of fracturing
- Bed thickness
- Hydrogeological parameters including aquifer properties, solution phenomena etc.
- Type and amount of overburden

Further detailed information can then be obtained in the laboratory using petrographic, mineralogical and physico-chemical techniques. Some of these investigative techniques and procedures are sophisticated and require expensively equipped laboratories; others are relatively simple and can be used in basic laboratories or even in the field setting. Figures 4 and 5 show flow diagrams summarizing laboratory assessment schemes for aggregate and chemical-grade limestones.

4.1 Petrographic techniques

The examination of rock slices, cut faces and thin sections with a petrological microscope can give a great deal of information on fabrics,
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textures and mineralogy. There are various levels of petrographic observation useful in limestone assessment and some require a more sophisticated approach than others. Observations may include:

- General lithology
- Palaeontology - identification of grain types
- Sedimentary and organic structures
- Colour variations
- Texture: size and shape sorting of grains
- Carbonate mineralogy
- Non-carbonate mineralogy
- Diagenetic observations - types of cement

Petrographical data should be referenced to either the Folk or Dunham classification systems for carbonate rocks (Figures 1 and 2). Detailed petrographic descriptions (including details of microfacies) are not always required for limestone resource assessments, although useful petrographic data can be easily obtained by adopting the techniques outlined below:

4.1.1 Sawing and polishing limestone slabs.

The interpretation of limestone fabrics is greatly assisted by simply cutting limestone blocks or core with a rock saw and studying the cut surface under a binocular microscope with reflected light. Observations are improved by wetting the sawn surface or, preferably, progressively polishing the surface with carborundum grit (F400, F600, and F1000 grades). Improved finishes may be obtained if polishing is continued with silica gel or fine diamond pastes.

4.1.2 Acid etching

The use of weak solutions of acids to etch sawn limestone core or blocks enables dolomite and non-carbonate impurities to be identified. It also emphasises the textural characteristics of the limestone. This is a simple procedure. Its value in petrographic logging and in the identification of non-carbonate minerals cannot be over-emphasised. It is a fundamental procedure in limestone resource appraisals.

Mineralogy and Petrology Group, British Geological Survey © NERC 1992
Limestone

Figure 4. Recommended procedure for the evaluation of the aggregate potential of carbonate rocks.

*Mineralogy and Petrology Group, British Geological Survey © NERC 1992*
Figure 5. Recommended procedure for evaluation of chemical-grade carbonate rocks.

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Limestone

Acetic acid (about 1 part concentrated acid to 5 parts water) will dissolve calcite but will not affect dolomite. Hydrochloric acid (about 1/10 Normal) will dissolve both minerals, but will more rapidly dissolve calcite, with the result that any rhombs of dolomite stand out clearly. Quartz or other siliceous impurities and any clay, bitumen, fluorite and pyrite will also be differentiated.

Etching is best carried out by immersing the sample face up in the acid solution. If the sample is face down, bubbles may be trapped, resulting in an uneven etch. The rate of etching depends on the strength of the solution, the temperature and the composition of the rock. The optimum etching time for each particular study must be determined by trial and error. For routine petrographical logging of limestone core or block samples, an etching time of around two minutes is recommended if a weak solution of HCl is used. A detailed procedure is given in Appendix 1.

4.1.3 Acetate peels

Peels are replicas of etched surfaces of carbonate rocks and are widely used in carbonate sedimentology for interpretation of carbonate textures and cements. They are not always required in limestone assessment programmes, but they are useful in the generation of a reference archive of carbonate lithologies.

Simple peels are easily made using commercial acetate film (0.005 inches or about 0.1 mm thickness) and acetone as solvent. A freshly etched and washed limestone specimen is flooded with acetone from a washbottle and the acetate film (cut to provide some overlap) is gently unrolled evenly across the surface. The lower side of the film is softened and, as the acetone evaporates, the film moulds itself to the textural irregularities of the rock. After drying for 10 to 15 minutes the film is peeled off, revealing a replica of the etched surface. Peels may be mounted in a book or between glass slides and can be stored as a reference archive.

The manufacture of high-quality peels requires considerable experience, and beginners should be prepared to practise with etching and drying times, staining etc. until acceptable results are consistently obtained. A detailed procedure is given in Appendix 2.

4.1.4 Staining

The staining of limestones to determine their carbonate mineralogy is a well-established technique (Dickson, 1966; Friedman, 1971; Allman and Lawrence, 1972). This technique is used primarily to determine the
Limestone

presence of dolomite, ferroan dolomite and ferroan calcite. Some staining methods may also successfully determine feldspars, gypsum, anhydrite, aragonite and clay minerals. The staining process induces a reaction on the surface of a particular mineral species which results in a coloured precipitate characteristic of that mineral.

The most useful stains for the assessment of carbonate rocks are:

- Alizarin red S in 30% NaOH. Stains Mg-calcite and dolomite purple.
- Alizarin red S in 1.5% HCl. Stains calcite and aragonite red. Stains ferroan dolomite and calcite purple.
- Potassium ferricyanide in dilute HCl. Stains all carbonates dark blue if they contain iron. Most dolomite is iron-rich, therefore this is a useful stain for distinguishing dolomite from calcite.
- Potassium ferricyanide and alizarin red S in 1.5% HCl. Stains calcite pink or red and ferroan calcite purple. Dolomite has no colour but ferroan dolomite is stained turquoise. This valuable dual staining technique allows differentiation between ferroan phases in calcites and dolomites to be carried out in one operation (Dickson, 1965, 1966).

It is recommended that the latter technique (potassium ferricyanide and alizarin red S in 1.5% HCl) is adopted for routine evaluation of carbonate deposits. A detailed procedure for this stain is given in Appendix 3.

4.1.5 Thin sections

Thin sections are the standard means of carbonate study and should be manufactured to a high specification. Sections cut for carbonate petrography should ideally be slightly thicker than 30 microns to obtain deeper colour contrast.

Instrumental techniques valuable in the petrographic study of carbonate rocks include Cathode Luminescence (CL) and Scanning Electron Microscopy (SEM). The former is useful in the study of crystal growth and cements and utilises the colour glow (luminescence) produced when a beam of low-energy electrons is focused on a thin section in a vacuum chamber. The SEM is used in detailed studies of cements and the composition of lime mud (micrite).
4.2 Chemical analysis

Many industrial applications of limestone require constraints on the levels of specific impurities (such as SiO₂, MgO and Fe₂O₃), and therefore chemical analyses of limestone raw materials are necessary to assess the grade of the stone. However, the carbonate content of limestone is fundamental in most industrial uses and a simple laboratory method for determining this component is a valuable procedure for determining chemical purity. Ideally the method should be rapid, simple, accurate and capable of giving reproducible results.

Recommended procedures for the systematic determination of carbonate content are outlined in Appendix 4.

The determination of carbonate content can then be used to classify chemical-grade limestones (Table 2). Such a definition of chemical purity is relatively simple and can be easily used to illustrate the distribution of limestone purity on a map. This classification is also suitable for comparison of chemical data for limestones of different geological origin.

Table 2. Classification of limestones by calcium carbonate content.

<table>
<thead>
<tr>
<th>Category</th>
<th>Percentage CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very high purity</td>
<td>&gt;98.5</td>
</tr>
<tr>
<td>High purity</td>
<td>97.0-98.5</td>
</tr>
<tr>
<td>Medium purity</td>
<td>93.5-97.0</td>
</tr>
<tr>
<td>Low purity</td>
<td>85.0-93.5</td>
</tr>
<tr>
<td>Impure</td>
<td>&lt;85.0</td>
</tr>
</tbody>
</table>

The classification of chemical-grade limestones by CaCO₃ content does not take account of all variations in chemical composition. Full chemical analyses should be carried out by X-ray fluorescence spectrometry (XRF) although wet chemical methods may be used where appropriate. A typical chemical analysis of limestone will include CaO, MgO, SiO₂, Al₂O₃, Fe₂O₃, Na₂O, K₂O, P₂O₅, MnO and S, F, Cu, Pb and Zn. For certain specialised end-uses it may also be necessary to analyse for As, Cr, Co or other trace elements. More detailed investigations may require
determination of the composition of individual carbonate components and/or associated minerals using electron beam instruments such as the microprobe or the SEM.

Chemical analyses of typical high-purity limestones are given in Table 3.

Table 3. Chemical analyses of some high-purity limestones.

These limestones are used, or have potential for use, in a wide range of industrial applications including glass manufacture, production of soda ash, sea water magnesia, sugar refining and high-grade fillers

<table>
<thead>
<tr>
<th></th>
<th>Derbyshire, UK¹</th>
<th>North Pennines, UK¹</th>
<th>Guanacaste, Costa Rica²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bee Low Limestone</td>
<td>Malham Formation</td>
<td>Barra Honda Limestone</td>
</tr>
<tr>
<td>(wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>55.09</td>
<td>55.54</td>
<td>55.71</td>
</tr>
<tr>
<td>MgO</td>
<td>0.37</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.64</td>
<td>0.26</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.05</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>A₁₂O₃</td>
<td>0.11</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>MnO</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.18</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Loss</td>
<td>43.44</td>
<td>43.40</td>
<td>43.70</td>
</tr>
<tr>
<td>(ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>100</td>
<td>0</td>
<td>414</td>
</tr>
<tr>
<td>Cu</td>
<td>4</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Zn</td>
<td>21</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>

1 Harrison et al. (1990)
2 Mathers et al. (1990)
Limestone

4.3 Mineralogical techniques

The mineral impurities commonly found in limestones include quartz, dolomite, clays, pyrite and other iron and manganese minerals. Characterisation of both carbonate and non-carbonate mineralogy can be initially undertaken by petrographical examinations of etched surfaces and thin sections as detailed above, although evaluations are generally enhanced by investigation of acid insoluble residues using optical microscopy and X-ray diffraction (XRD). When residues are retained on filters (ideally small nitro-cellulose type filters) they are easily examined under a binocular microscope or mounted for XRD studies. Laboratory procedures for the preparation of acid insoluble residues are given in Appendix 4.

4.4 Physical and mechanical property testing

In addition to assessment of chemical and mineralogical characteristics, an evaluation of limestone for multipurpose applications must also consider certain physical and mechanical properties of the stone. Strength and durability are of prime importance in assessment for aggregate use (in concrete or as roadstone), together with other properties such as specific gravity and water absorption. Frost susceptibility and the porosity of the stone are important properties in the assessment of limestone for use as dimension stone. Particle size distribution and colour of the powder are important properties in the evaluation of limestone powders, together with such parameters as surface area and degree of oil absorption. Assessment of limestone for lime will involve determination of lime-burning performance. This may include measurement of surface area and reactivity of the lime, together with the degree of decrepitation of the stone. A wide range of physical and mechanical properties need to be considered in laboratory limestone investigations and the degree to which they are each investigated depends on the intended end-use of the raw material.

4.4.1 Testing procedures for aggregates

Detailed procedures for testing aggregate properties are described elsewhere in this series of manuals. Methods commonly applicable to testing limestone raw materials for aggregates are outlined in Table 4. Most of these procedures are to BS 812: 1990. Some typical results for limestone aggregates from the UK are shown in Table 5.

Where testing or sample preparation facilities are limited, it is recommended that testing procedures are restricted to the AIV test (or similar) or to the LAAV test. Values of relative density and water absorption should also always be obtained.
Limestone

Table 4. Test procedures for limestone aggregates.

<table>
<thead>
<tr>
<th>Physical tests:</th>
<th>Mechanical Tests (strength and durability):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flakiness index.</td>
<td>Aggregate impact value (AIV). Measures resistance to granulation</td>
</tr>
<tr>
<td>Relative density.</td>
<td>under impact stresses</td>
</tr>
<tr>
<td>Water absorption.</td>
<td>Aggregate crushing value (ACV). Measures resistance to crushing</td>
</tr>
<tr>
<td></td>
<td>under a gradually applied load</td>
</tr>
<tr>
<td></td>
<td>10% fines value. Measures resistance to crushing by the application</td>
</tr>
<tr>
<td></td>
<td>of a continuous load</td>
</tr>
<tr>
<td></td>
<td>Los Angeles abrasion value (LAAV). Measures resistance to attrition</td>
</tr>
<tr>
<td></td>
<td>by impact and abrasion forces (this test is not in BS 812 but is</td>
</tr>
<tr>
<td></td>
<td>internationally recognised (ASTM C131))</td>
</tr>
<tr>
<td></td>
<td>Aggregate abrasion value (AAV). Measures surface wear following</td>
</tr>
<tr>
<td></td>
<td>abrasion</td>
</tr>
</tbody>
</table>

Table 5. Typical aggregate property data of Carboniferous Limestones from two regions on the UK.

<table>
<thead>
<tr>
<th>Carboniferous Limestone</th>
<th>Carboniferous Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mendip Hills</td>
<td>Derbyshire</td>
</tr>
<tr>
<td>AIV 18 to 21</td>
<td>20 to 25</td>
</tr>
<tr>
<td>ACV 20 to 24</td>
<td>20 to 30</td>
</tr>
<tr>
<td>AAV 7.5 to 10.1</td>
<td>8.0 to 15.0</td>
</tr>
<tr>
<td>LAAV 22 to 24</td>
<td>21 to 27</td>
</tr>
<tr>
<td>Relative Density 2.65 to 2.71</td>
<td>2.68 to 2.72</td>
</tr>
<tr>
<td>Water Absorption (%): 0.40 to 0.80</td>
<td>0.10 to 1.50</td>
</tr>
</tbody>
</table>

After Harrison & Adlam (1985); Harrison et al. (1992).

Note: These limestones are widely quarried for roadstone and concreting aggregates. Most good quality limestone aggregates should be expected to give similar test values.
Limestone

4.4.2 Test procedures for dimension stone

Limestone used for structural walls or for decorative cladding should be durable in the prevailing climatic and environmental conditions. Durability is principally determined by the physical structure of the stone, particularly pore structure. There is no British Standard durability test for limestones, although a number of procedures for assessing pore structure and for determining the likely in-service performance of limestones are commonly used.

Laboratory tests can be divided into two categories: direct measurement of degradational processes and indirect measurement of pore structure. The former includes tests to determine load bearing (ASTM C99, C170), wear (C241) and salt crystallisation (BRE 1983, 1989). Indirect measurements of pore structure include determinations of porosity, saturation coefficient and sonic velocity. A summary of ASTM specification requirements for dimension stone is given in Table 6.

<table>
<thead>
<tr>
<th>Density Mg/m³ (min)</th>
<th>Absorption % (max)</th>
<th>Modulus of rupture MPa (min)</th>
<th>Compressive strength MPa (min)</th>
<th>Abrasion resistance (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High density limestone</td>
<td>2.56</td>
<td>3</td>
<td>6.9</td>
<td>55</td>
</tr>
<tr>
<td>Medium density limestone</td>
<td>2.16</td>
<td>7.5</td>
<td>3.4</td>
<td>28</td>
</tr>
<tr>
<td>Low density limestone</td>
<td>1.76</td>
<td>12</td>
<td>2.9</td>
<td>12</td>
</tr>
</tbody>
</table>

The pore structure of a potential dimension stone may be assessed by determination of porosity and saturation coefficient (the extent to which the pores fill with water with time). These two parameters indicate the amount of water a stone will absorb under natural conditions. Most limestone decay is caused by gypsum crystallisation resulting from a reaction between air, water and the limestone. The expansion which takes place during the precipitation of gypsum may cause the stone to fail. The BRE crystallisation test is a form of aggressive accelerated weathering. In brief, the test involves immersion of dry stone cubes in...
Limestone

a solution of sodium sulphate decahydrate for two hours at a constant temperature. This is followed by oven drying at controlled humidity for 16 hours. After cooling, the process is repeated for a total of 15 cycles. The results are presented as a percentage weight loss and have been used to divide limestones into six classes of durability (Honeybourne, 1982). These classes are summarized in Table 7 and range from grade A (best) to grade F (worst). A detailed procedure for this test is given in Appendix 5.

Table 7. Durability grades of limestone building stones (after Honeybourne, 1982).

<table>
<thead>
<tr>
<th>Limestone durability grade</th>
<th>% Weight loss (crystallisation test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>B</td>
<td>1 - 5</td>
</tr>
<tr>
<td>C</td>
<td>5 - 15</td>
</tr>
<tr>
<td>D</td>
<td>15 - 35</td>
</tr>
<tr>
<td>E</td>
<td>35 - 100</td>
</tr>
<tr>
<td>F</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>

The BRE recrystallisation test requires relatively sophisticated laboratory facilities and is expensive and time consuming. The results cannot always be interpreted with confidence since the test can prove unreliable. However, it is the most widely accepted test for the durability of porous building stones. It is recommended that additional indirect studies of pore structure be carried out to evaluate durability.

4.4.3 Testing procedures for limestone fillers

Determination of particle-size distribution, colour and oil absorption are generally necessary in the assessment of limestone powders for use as fillers in paper, paint, plastic and other materials. A full discussion of the assessment of limestones for use as fillers is given elsewhere in this series of manuals.

Particle size distribution is controlled by the inherent strength of the limestone and by the degree of processing (grinding) and is generally determined by a combination of dry sieving and sedimentation. Colour
Limestone

is of prime importance in filler applications, and in almost all instances the filler must be consistently white. There are several ways of measuring whiteness and most require relatively sophisticated instrumentation. A relatively simple method for comparative brightness measurement is used by BGS and a detailed procedure is given elsewhere in this series of manuals. Powders (whitenings) used as pigments in the paint industry are required to have low oil absorption. Values of oil absorption reflect the quantity of oil absorbed on the particle surfaces and the quantity required to fill the voids between the particles.

4.4.4 Testing procedures for lime

The production of high-quality lime depends on calcination conditions and on the nature of the raw material. The quality of lime is usually assessed by measuring its reactivity and surface area, although other factors such as its porosity, bulk density, loss on ignition and strength may also be evaluated. In addition, the tendency of the stone to decrepitate during calcination is also usually investigated.

The aim of a laboratory investigation is to monitor the quality of lime produced as a function of temperature. Representative samples of limestone are generally shock calcined (placed in a pre-heated furnace) at a range of temperatures from 850°C to 1100°C. This allows the relationship between calcination temperature, surface area, reactivity and decrepitation index to be examined. A flowsheet which details a typical laboratory scheme for the investigation of lime reactivity, decrepitation and surface area is given in Figure 6.

Calcination temperature, surface area and reactivity

The production of good quality lime depends largely on the type of kiln, conditions of calcination and the nature of the limestone/dolomite raw material. At relatively low calcination temperatures, products formed in the kiln contain both unburnt carbonate and lime and are said to be 'underburnt'. As calcination temperature increases, 'soft burnt' or 'high reactive' limes are produced, followed at still higher temperatures by 'dead burnt' or 'low reactive' limes. Overall suitability of a limestone for lime production and appropriate temperature of calcination may be ascertained by determination of physical properties of lime produced at different calcination temperatures in the laboratory.

At the onset of calcination of limestone, calcium carbonate on the surface of the chippings begins to decompose as follows:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
Limestone

Figure 6. Flowsheet for a typical laboratory scheme for lime testing.
Limestone

Dolomite follows a similar reaction:

$$\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaO.MgO} + 2\text{CO}_2$$

The MgCO$_3$ component in dolomite decomposes at a slightly lower temperature than the CaCO$_3$.

As calcination proceeds, a decomposition reaction front gradually migrates toward the core of the chippings. The reaction front forms a boundary between an outer shell of lime and an unburnt core of carbonate. Carbon dioxide formed at the reaction front is released through pores in the surrounding lime shell. The rate of decomposition is controlled primarily by the amount of heat energy reaching the unburnt core, and by the rate of diffusion of carbon dioxide from the reaction front. Thus, at a given firing temperature, the unequal rates of burning which may be exhibited by samples are due to textural differences; dense, coarsely crystalline carbonate rock is relatively slow-burning as the escape of carbon dioxide is impeded by closely-packed, large lime crystals, whereas a fine-grained rock is relatively quick-burning as carbon dioxide diffuses rapidly through the large number of pores between small lime crystals.

In samples that are fired at an insufficiently high temperature, or are particularly slow-burning, the carbonate decomposition front will not reach the core of the chippings and a lime product containing unburnt carbonate as well as lime will be produced.

A 'high reactive' or 'soft-burnt' lime is produced when the reaction front reaches the cores of the chippings and converts all carbonate present to lime. A 'high reactive' product is relatively soft, contains small lime crystallites and has an open porous structure with an easily accessible interior. A lime of this type has the optimum properties of high reactivity, high surface area and low bulk density. Increasing the degree of burning beyond this stage (either by increasing calcination temperature and/or duration of calcination) is detrimental, since lime crystallites already formed will tend to grow larger, agglomerate and sinter. This results in a decrease in surface area, porosity and reactivity, and an increase in bulk density. The denser, less reactive product formed is known as 'dead-burnt' or 'low reactive' lime.

Dolomitic limes are generally less reactive than equivalent high-calcium limes because of the tendency of the MgO component to 'dead-burn'. This occurs because MgO forms from dolomite at a lower temperature than CaO and so crystallites tend to grow larger and less reactive. This has a profound effect on the hydration or slaking behaviour of dolomitic limes.
Limestone

The degree of reactivity of a lime is particularly important in the metallurgical industry. This property is normally measured by the rate of the lime hydration (slaking) reaction. This reaction is exothermic and the rate of reaction is related to the surface area exposed to hydration and accessibility of water to the interior of the lump. It is evaluated by a relatively simple slaking test (ASTM C110-76a) which measures the heat of hydration produced by a known weight of lime in a known volume of water over two minutes. Details of a modified version of this test used in BGS laboratories are included in Appendix 6.

Lime reactivity, porosity, surface area and bulk density are all inter-related properties of unhydrated lime. Reaction rate of lime with water is mainly a function of available surface area; porosity is directly related to surface area and inversely proportional to bulk density. Surface area of unhydrated lime may be determined using the single-point nitrogen BET technique. Appendix 7 gives information on preparation of unhydrated lime samples for surface area analysis using this instrumental technique.

Decrepitation Decrepitation of a limestone is a measure of its susceptibility to disintegration during calcination. Closely-sized limestone feed is necessary for the efficient operation of many industrial kilns, particularly shaft kilns. Feed of a narrow size range forms a porous bed that allows the passage of hot gases during calcination. Decrepitation decreases the porosity of the bed, impeding the flow of gases and reducing efficiency. In general, there is a positive correlation between the degree of decrepitation and crystal size in a carbonate rock. Coarsely crystalline limestones and marbles show a greater tendency to decrepitate than finer grained material. Fine particles of lime are unacceptable in some industrial applications. A simple test to measure the tendency of a stone to decrepitate can be undertaken by sieving the calcined material and weighing the material passing relative to the total weight to give the percentage decrepitation. A procedure for this test is included in Appendix 6.

Interpretation of lime testing results Surface area, reactivity and decrepitation determinations carried out on limestone calcined at a variety of temperatures should enable changes in lime quality to be monitored and optimum calcination temperature determined. These results can then be compared to those obtained from limestone of proven quality as lime raw materials. Table 8 gives physical property data on surface area, reactivity and decrepitation resulting from tests on unhydrated lime derived from limestones from Costa Rica and Zimbabwe. These data are compared to high-quality limestones from the UK which are used as raw material for lime manufacture.
Limestone

Table 8. Physical properties of unhydrated lime made from limestones from Costa Rica, Zimbabwe and the UK.

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>Sample</th>
<th>Decrepitation (wt %)</th>
<th>Surface area (m²/g)</th>
<th>Reactivity 120 sec (°C/250 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>JB 7</td>
<td>0.5</td>
<td>4.56</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>Z MQ</td>
<td>27.06</td>
<td>3.2</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>UK C</td>
<td>0.22</td>
<td>1.6</td>
<td>4.0</td>
</tr>
<tr>
<td>950</td>
<td>JB 7</td>
<td>2.7</td>
<td>5.18</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>Z MQ</td>
<td>15.21</td>
<td>3.4</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>UK C</td>
<td>4.0</td>
<td>3.4</td>
<td>16.9</td>
</tr>
<tr>
<td>1000</td>
<td>JB 7</td>
<td>0.5</td>
<td>5.15</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>Z MQ</td>
<td>25.58</td>
<td>1.4</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>UK C</td>
<td>5.56</td>
<td>4.3</td>
<td>21.9</td>
</tr>
<tr>
<td>1050</td>
<td>JB 7</td>
<td>8.3</td>
<td>2.83</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>Z MQ</td>
<td>26.60</td>
<td>0.4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>UK C</td>
<td>6.94</td>
<td>2.5</td>
<td>21.8</td>
</tr>
</tbody>
</table>

The use of overlay plots (Figure 7) allows comparison of lime burning performance between related groups of limestone samples. The relationship between mean crystallite size (as measured from thin sections) and surface area/reactivity/decrepitation may also be used for comparison between samples and groups of samples. The plots show similar behaviour between samples UK C (a limestone mined commercially in the UK) and JB 7 (a high-purity limestone from Costa Rica). Both limestones show maximum reactivity and surface area developing around 1000°C; beyond this temperature both parameters begin to fall as the lime becomes 'dead-burnt'. The behaviour of these relatively fine-grained limestones contrasts with that of Z MQ (a coarsely crystalline metamorphic limestone from Zimbabwe). This material develops maximum surface area and reactivity at a lower temperature. It also shows a much greater tendency to decrepitate. This contrasting behaviour on calcination is typical when comparing dense, fine-grained limestones (generally most suitable for lime making) with coarsely crystalline metamorphic carbonates (generally least suitable).

These tests should enable an optimum calcination temperature to be established for each limestone examined. The lime-burning performance of different samples and groups of samples can be compared and related to mineralogy, petrography and chemistry.

Mineralogy and Petrology Group, British Geological Survey © NERC 1992
Limestone

Figure 7. Overlay plots showing relationship between physical properties of unhydrated lime and calcination temperature.
Limestone

REFERENCES


British Standards Institution (1983) Aggregates from Natural Sources for Concrete, BSS 882.


Limestone


Limestone


Appendix 1: Acid etching.

Several reagents are available for etching carbonate minerals but cold dilute hydrochloric acid (about 5 - 10% by volume) is appropriate for general petrographic study. Rubber gloves should be worn throughout this operation.

1. Pour the etching solution in a large glass or plastic tray and place the rock slice face up in the solution.

2. Gently agitate the acid with a glass rod to prevent formation of bubbles.

3. The etching time may be varied from 1 minute to over 5 minutes but about 2 minutes is the recommended time.

4. Flush the etched rock slice in cold water (in a bucket or sink).

5. The etched surface is now ready for examination by binocular microscopy.
Appendix 2: Preparation of acetate peels.

1. Lightly etch the rock slice in 10% N HCl for a maximum of 1 minute and wash in water.

2. Flood the prepared etched surface with acetone from a wash bottle.

3. Quickly roll on to the surface a sheet of acetate film (0.1 mm thick) which has previously been cut to size (with about 1cm overlap). Spread the film on evenly to prevent entrapment of air bubbles.

4. Let the peel dry for around 15 minutes and then peel it off.

5. Mount the peel between glass slides (to prevent wrinkling) or store between the pages of a thick book.

6. Peels can also be taken off stained surfaces starting at Stage 2 above.
Appendix 3: Limestone staining procedure.
Potassium ferricyanide and Alizarin Red S in 1.5% HCl.

1. Immerse sample in etching solution (dilute HCl at room temperature) for approximately 15 seconds. NB: the success of the staining depends on the quality of the etch; cold solutions give poor results; weak etching gives a patchy stain; and over-etching produces a very dense stain.

2. Immerse sample in combined staining solution. This consists of 3:2 mixture of dye (0.2g Alizarin Red S dissolved in 100 ml 1.5% HCl) and ferricyanide (2g of potassium ferricyanide dissolved in 100 ml 1.5% HCl) for 30-35 seconds. NB: solutions must be freshly made for each staining session.

3. Wash stained sample gently in distilled water and dry in a stream of warm air.

CAUTION. Cyanide is poisonous - use rubber gloves throughout procedure.

Staining is usefully employed on sawn block or core samples, peels (the peel takes up the colour of the stained surface) and thin sections. The success of staining depends on staining times, solution strength, age of reagents and temperature.
Appendix 4: Determination of carbonate content and preparation of insoluble residues.

Loss on ignition

By heating powdered samples of limestone in a laboratory muffle furnace, the loss of weight due to release of CO₂ can be used to calculate the percentage CaCO₃ content.

The procedure for determination of carbonate content by loss on ignition is as follows:

1. Grind samples to a powder passing a 63 μm sieve.
2. Weigh a 2 g sample into a platinum crucible and dry in a laboratory oven for one hour at 105°C.
3. Record dried weight.
4. Place samples in a muffle furnace at 550°C for 25 minutes.
5. Remove, cool in a desiccator and weigh.
6. Calculate weight loss due to release of carbonaceous material and water.
7. Return samples to muffle furnace and increase temperature to 1000°C.
8. Leave samples for one hour at 1000°C, remove, cool in a desiccator and weigh.
9. Calculate loss in weight between 550°C and 1000°C.

\[
\% \text{ CaCO}_3 \text{ content} = \frac{\% \text{ wt loss}}{44\%} \times 100
\]

The theoretical weight loss of pure calcium carbonate is 44%. Greater values may result when the rock contains carbonate minerals other than calcite. Pure dolomitic limestone will give a greater loss than limestone since the mineral dolomite loses 48% of its weight as CO₂. If the presence of dolomite is suspected, then 48% should be substituted in the above equation. This will give a minimum carbonate value for rock containing a mixture of calcite and dolomite.
Appendix 4 (continued)

This simple and rapid technique gives relatively accurate results, particularly for limestones which are free of other carbonates. Further information is given by Kannie Galle & Runnel (1960).

Insoluble residue

This procedure involves the digestion of limestone samples in dilute acid to determine weight loss by CO₂ evolution and has the merit of providing samples of the non-carbonate fraction (insoluble residue) for mineralogical examination. There are two standard methods for insoluble residue determinations.

Rock chip method

1. Separate a representative 25 g sub-sample of rock chips (10 mm nominal size) using a sample splitter.
2. Weigh accurately (M₁) and place in a beaker. Place beaker in a fume cupboard.
3. Add dilute HCl (about 10% N) slowly, to cover chips.
4. Add acid until bubbling ceases.
5. Weigh a filter paper, place in a funnel and filter the acid insoluble residue.
6. Dry the filter paper and residue in an oven at 105°C for several hours.
7. Weigh the filter paper and residue.
8. Calculate the weight of residue or non-carbonate content (M₂).
9. Calculate the percentage residue by using the formula:

   \[ \frac{M₂ \times 100}{M₁} = \% \text{ residue} \]

10. Carbonate content = 100% - % residue
Appendix 4 (continued)

This technique is extremely simple and is particularly suited for basic laboratory facilities and can even be adapted for use in the field. Care must be taken to ensure all carbonate is dissolved, all reaction salts are removed by washing, and residue is not lost during filtering. Dolomite dissolves slowly in a cold acid solution. If dolomite is present, then the acid solution should be warmed on a hot plate to about 70°C.

Limestone powder method

The second method involves a slightly more complicated laboratory procedure based on the analysis of small samples of limestone powder.

1. Weigh a small nitrocellulose filter accurately to four decimal places.
2. Place powder (<63 μm particle size, subsampled using a sample splitter) on filter disc (still on balance) and record weight accurately to four decimal places. Use a powder weight of about 1 g.
3. Transfer filter and powder to filter holder on top of vacuum flask apparatus. The flask is connected to a vacuum pump.
4. Add dilute HCl (10% N) until bubbling ceases.
5. Drain filter with vacuum.
6. Wash residue and holder with distilled water and filter with vacuum. Repeat.
7. Remove filter disc and dry in oven at 105°C or air-dry for several hours.
8. Weigh filter and insoluble residue.
9. Calculate carbonate percentage (as in 'rock chip' method above).

This method permits rapid and accurate analysis of calcium carbonate and combines this with high throughput. Detailed technical procedures are given by Cox (1977) and Molnia (1974).
Appendix 5: Procedures for testing dimension stones.

Porosity

Samples of building stone are dried and weighed \( (W_o) \) and then saturated with water under vacuum (Price, 1975). They are then weighed in water \( (W_1) \) and again in air \( (W_2) \), and the porosity \( (P) \) is calculated as follows:

\[
P = \frac{W_2 - W_o}{W_2 - W_1} \times 100 \%
\]

The porosity is thus defined as the volume of a stone's pore space expressed as a percentage of the stone's total volume.

Saturation coefficient

The saturation coefficient is a measure of the extent to which the pores are filled when a stone absorbs water for a standard time. Once the porosity has been measured, the sample is dried, immersed in water for 24 hours and weighed \( (W_3) \).

The saturation coefficient \( (S) \) is then calculated:

\[
S = \frac{W_3 - W_o}{W_2 - W_o}
\]
Limestone

Appendix 5 (continued)

BRE crystallisation test

1. Make up sodium sulphate solution (by dissolving 1.4 kg of sodium sulphate decahydrate in 8.6 litres of water) at 20 ± 0.5°C.

2. Prepare between four and six 4 cm diameter cubes of the stone using a suitable saw.

3. Wash and dry at 103 ± 2°C.

4. Allow to cool in a desiccator to 20 ± 2°C.

5. Weigh cubes to ± 0.01 grams (W₀).

6. Label and weigh them again (W₁).

7. Place each cube in a 250 ml beaker and cover with sodium sulphate solution to a depth of 8 mm. Leave for 2 hours, keeping at 20 ± 0.5°C.

8. Remove cubes from solution and place in an oven at 103°C ± 2°C. The oven should be initially humid by placing a shallow tray in the oven containing 300 ml of water, 30 minutes before adding the test cubes. Dry for 16 hours.

9. Remove cubes and allow to cool to 20 ± 2°C.

10. Repeat steps 7 to 9 until 15 cycles have been completed.

11. Weigh the cubes (Wₐ).

   Calculate the percentage weight loss:

   \[ \% \text{ weight loss} = 100 \left( \frac{Wₐ - W₂}{W₀} \right) \]

12. Calculate the mean percentage loss.
Appendix 6: Determination of decrepitation and reactivity of unhydrated lime.

Calcination and determination of decrepitation

1. Jaw-crush raw limestone to between 20-10 mm. Material < 10 mm should be screened out.

2. Preheat furnace to selected calcination temperature and record (a).

3. Weigh empty crucible (b).

4. Place approximately 120 g limestone in crucible and record crucible + raw sample weight (c).

5. Calculate raw sample weight (d).
   
   \[ c - b = d \]

6. Place sample in preheated furnace and record time.

7. After 1 hour, remove crucible and place in desiccator to cool.

8. When crucible is cool enough to be picked up by hand, weigh sample + crucible and record (e).

9. Calculate weight of calcined sample (f).
   
   \[ e - b = f \]

10. Calculate % loss on ignition (LOI) (g).

   \[ \frac{|d - f|}{d} \times 100 = \% \text{ LOI} \ (g) \]

11. Tip crucible contents on to 4 mm screen placed on paper sheet. Tap screen on bench five times from a height of approximately 5 cm.

12. Weigh material passing 4 mm screen (h).

14. Calculate % decrepitation (i).

   \[ \left(\frac{h}{f}\right) \times 100 = \% \text{ decrepitation} \ (i) \]

15. Recombine <4 mm and >4 mm fractions and bag (this material can be used for the reactivity test and surface are determination).
Limestone

Appendix 6 (continued)

16. Note colour of lime and any other salient features.

Notes. Determination of carbonate using this method is only valid for calcination temperatures including and greater than 900°C. Calcined limestone may be stored in a desiccator for two to three days without significant deterioration. Exercise care in handling unhydrated lime (quicklime), as it is capable of causing burns. Do not breath dust.

Lime reactivity test

1. Calculate water volume required (vol. [ml] = 6 x calcined limestone wt) and record (c).
2. Add water to 1 litre beaker and set stirrer as close to base of beaker as possible without contact. Immerse thermometer to a depth of approximately 2 cm. Ensure that the thermometer can be read easily and that the bulb is in complete contact with water.
3. Set stirrer speed to 300 rpm.
4. Record water temperature (d).
5. Set stopwatch running and immediately add the calcined limestone to water.
6. Record water temperature after 5, 10, 15 and 30 second, and 1 and 2 minutes.
7. Calculate temperature change (Δ t) for each time point and record.
8. Plot Δ t against time on time/temperature diagram.
9. Note colour and general appearance of hydrated lime (are there any lumps of raw limestone in the bottom of the beaker?).

Notes Take care when adding unhydrated lime to water, as this is a violent, exothermic (heat-producing) reaction.
Appendix 7: Surface area determination (BET method).

Using the BET method, surface area measurement of powdered solids is carried out by determining the quantity of gas that adsorbs as a single layer of molecules on the surface of a sample (a monomolecular layer or monolayer). The BET instrument employed in BGS laboratories uses a 30% nitrogen: 70% helium gas supply to obtain a single-point value for surface area expressed in m²/g.

Consistent sample preparation is important for obtaining reproducible surface area values from unhydrated lime calcined at a range of temperatures. Prior to analysis, samples are purged of any gases or vapours present (especially water vapour). Gases and vapours, if present, occupy space on the surface of a sample that then cannot take up adsorbate gas during the analysis. A true surface area value is obtained only when these volatile components are removed.

Sample preparation and analysis

Care must be exercised in sampling unhydrated lime for surface area measurement. It is particularly difficult to obtain representative samples from material containing unburnt limestone (generally those calcined at temperatures below 950°C). It is recommended that at least 10g of calcined lump material is crushed to less than 250 μm prior to sampling. This should ensure that the 1 g subsample for surface area measurement is reasonably representative. The crushing and screening process must be carried out quickly since the unhydrated lime will rapidly absorb water from the atmosphere. All calcined samples must be stored in a desiccator. Reproducible surface area results from unhydrated lime obtained by degassing subsamples overnight at 110°C in a vacuum oven, followed by 1 hour on the BET instrument degassing station immediately prior to analysis.

Because the single-point surface area measurement method and calibration technique are general specific to the particular instrument used, detailed procedures are not appropriate in this manual.