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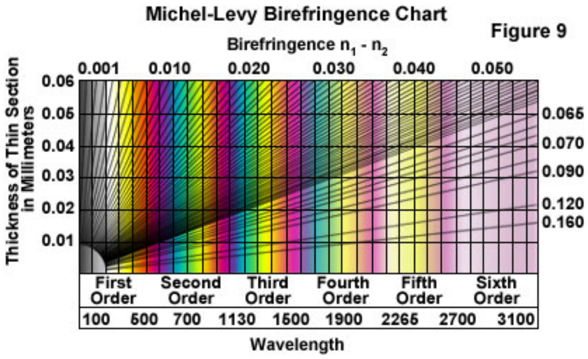

<u>Michel-Levy chart – for optical mineralogy study</u>

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<u>PHYSICAL AND CHEMICAL PROPERTIES OF LIMESTONE – DICTATING THE APPLICATION LIMIT</u>

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PHYSICAL AND CHEMICAL PROPERTIES OF LIMESTONE – DICTATING THE CHOICE OF MATERIALS

2.1 INTRODUCTION

Although a limestone deposit may be located close to market and amenable to surface mining, it is the geology that ultimately determines the material's usefulness for exploitation. Geologically, there are many different types of limestone, formed in different environments by a variety of mechanisms, and understanding their formation is a useful guide when considering the location of carbonate deposits and their utilisation. The environment of deposition and subsequent mineralogical and tectonic changes are significant factors that determine the eventual size, shape, chemical purity and physical characteristics of each limestone deposit. There are big differences between the chemical compositions and physical properties, so not all limestone deposits are suitable for production (e.g. for GCC and lime production) required by today's industries. Most calcium carbonate raw material is derived from limestone, chalk or marble and, to a lesser extent, vein calcite, dolomite, aragonite, carbonatite and travertine.

Product specifications play an important role in determining the choice of materials for a particular application in industry. **The uses of a limestone depend on its physical properties, mechanical properties, chemical properties or a combination of all three**. There are relative levels of chemical impurities, which usually restrict the generally high purity grade calcium carbonates (minimum content of 97%). Silica and chert are the most common types of impurity, occurring as disseminated grains or as concentration of nodules, lenses, or beds. Organic matter can also cause problems, as can the varying degrees of dolomitisation which may exist.

Dolomitization.

Dolomitization is a diagenesis proses: a chemical or physical change undergone by a sediment after its initial deposition. Diagenesis of **limestone into dolomite**- involves the substitution of some Ca^{2+} ions in limestone ($CaCO_3$) by Mg ions to form dolomite ((Ca, Mg)CO_3). - **dolomitization** is usually a result of the percolation of Mg^{2+} rich waters (sea water) through limestone during which some Ca^{2+} ions in $CaCO_3$ are substituted for by Mg^{2+} ions.

- Mg^{2+} is abundant in natural waters so why doesn't **$MgCO_3$** precipitate along with $CaCO_3$ from natural waters?

- **reason:** Mg^{2+} is much smaller than Ca^{2+} and, therefore, its association with dipolar water molecules (hydration) is much stronger than for Ca^{2+}. It's significantly more difficult to strip off H_2O from Mg^{2+} ions than from Ca^{2+} ions. Therefore, it is more difficult to precipitate $MgCO_3$ than $CaCO_3$ from solution. However, a higher temperature experienced during the burial of limestone, thermal energy makes it easier for Mg^{2+} ions to participate in crystallization (where it replaces some of the Ca^{2+} ions in the $CaCO_3$ structure).

- **dolomitization is a secondary process** (dolomite crystals are often seen intruding into calcite crystals). Most dolomitization occurs in ancient limestone deposits (very little dolomitization in younger limestones).

Calcium carbonate is available all over the world, but there are big differences between the chemical compositions and physical properties of this material. A limestone deposit may be amenable to surface mining, and located close to markets, but it is the geology which ultimately determines the usefulness of limestone. The uses of limestone depend mainly on physical and chemical properties of the rock and its derived products. Chemical and physical properties are often interrelated; for instance, chemically pure limestone usually exhibits excellent whiteness appearance, compared to carbonaceous contaminated material. Those property requirements play an important role in dictating the choice of materials for particular applications. Physical and mechanical properties are important criterion for limestone in the construction sector and fillers, whereas chemical properties are vital where the stone is to be used as a chemical reactive ingredient (Power, 1985, Bristow, 1992, Andrew and Vagt 1993; and Matter, 1996)

The presence of even relatively small proportions of chemical impurities in high-grade limestone may restrict the uses of the material for certain applications. These impurities can be homogeneous or heterogeneous within the rock mass. Silica and alumina (in the form of clay, silt and sand), limonite and pyrite are commonly found as heterogeneous impurities in features such as joints and bedding planes. Homogeneous impurities are usually difficult to remove and include dissolved substances such as carbonaceous matter, iron carbonate, trace elements and other calc-silicates.

Those introduced heterogeneously generally can be reduced by washing or screening, or complicated processing such as flotation, but these are impractical to remove homogeneous impurities like sulphides, chlorite and graphite. Other current methods employed include electrostatic separation and photochemical separation.

Although, Malaysia possesses plentiful resources of limestone, there is a lack of valuable scientific data to provide useful fundamental guidance necessary for resource development for a high quality and value added product. Availability of scientific data is always routine in nature and is often restricted to in house for commercial appraisal purposes by certain private enterprises, rather than research and development (R & D) as a whole. Investigations undertaken should go beyond fundamental characterisation of the material and denoting the resource for regional and industrial development plan purposes only.

Therefore, the evaluation of a limestone resource for potential multi-purpose applications, must involver more than geological survey. **It is necessary to determine the mineralogical, chemical, physical and mechanical properties of the material and compare these properties with specification for each end use**. Furthermore, the type of feasibility study required must also include sufficient testing of the commercial parameters of end-products to demonstrate that these products could be economically produced and would be acceptable to the user industries. The most meaningful are commercial tests used by consuming industries for quality control, or in accordance with international standards (ISO).

2.2 Chemical Characterisation

The technological future of $CaCO_3$ lies in the chemistry. The carbonate content of limestone is fundamental in most industrial uses in determining the chemical purity of the resources, and is the basis for chemical grade limestone classification (*Table 2.1*). This 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 of different geological origins. However, the classification of chemical-grade limestones by $CaCO_3$ content does not take account of all possible variations and potential applications.

***Table 2.1* : British Geological Scheme for the classification of limestone by purity (*after Harrison, 1992*).**

No	Percentage of		Category
	$CaCO_3$	Equivalent CaO	
1	> 98.5	> 55.2	Very high purity
2	97.0 – 98.5	54.3 – 55.2	High purity
3	93.5 – 97.0	52.4 – 54.3	Medium purity
4	85.0 – 93.5	47.6 – 52.4	Low purity
5	< 85.0	< 47.6	Impure

Loss-on-ignition and acid insoluble residue are also used, but the latter is recommended for systematic resource investigations, as it is very simple and has the advantage of high rates of sample throughput (Harrison, 1992). The presence of very small amounts flint, silica, fuel ash and similar materials for many uses is unacceptable. These impurities are generally insoluble in dilute acids. In this determination, the proportion of materials insoluble in dilute acetic or hydrochloric acid is determined. The acid-insoluble residue of a typical limestone consists of free silica and a mixture of minerals such as clays, mica, feldspar, tourmaline, barytes, garnet, zircon, rutile, or other refractory materials. Many industrial applications of limestone require limits on the levels of specific impurities (e.g. SiO_2, MgO and Fe_2O_3), and therefore throughout chemical analysis is necessary to assess the chemical grade of rock. The proportion of silica (SiO_2) and alumina (Al_2O_3) in limestone deposit may be helpful in determining the economic value of the limestone for a use in which chemical properties are important. When clay minerals are present, as much as 2.0% silica may be accompanied by 1.0% alumina. The alumina content can be multiplied by two to obtain an estimate of the amount of silica in the clay (Andrew and Vagt, 1993). For example, silica must be kept to a minimum as its abrasive nature can damage the various moulds and dies in the performing process of plastics and papermaking. In lime manufacturing, SiO_2 not only acts as an impurity, but also reacts with CaO to form a dicalcium carbonate, consuming two molecules of CaO for every one of SiO_2 (Oates, 1998). According to this reaction, a limestone with 2.0% SiO_2 may theoretically result in a lime containing a maximum of only 90% CaO, as once calcination is underway, the 2.0% SiO_2 is increased to around 4%, due to the weight lost by the release of CO_2, and this 4.0% could react with 8.0% of the CaO to a form bicalcium silicate phase. Higher percentage of MgO can reduce the efficiency of energy required in the grinding, because of its higher crushing strength.

Therefore, it is essential that rapid and reproducible analyses results are required especially for determining chemical purity, where the presence of specified elements and impurities should be maintained at the minimum level required for a particular application. Detailed chemical analyses are carried out by X-ray fluorescence spectrometry (XRF), atomic absorption spectrometry (AAS) an other conventional wet chemical methods. A typical chemical analysis of limestone will include CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, P_2O_5, S, F, Cu, Pb and Zn. For certain specialised end uses, analyses for As, Cr, Co or other trace elements may also necessary.

2.3 Physical and Mechanical Properties

The physical and mechanical properties of a limestone determine many industrial applications. An evaluation of limestone for multipurpose applications must also consider certain physical and chemical properties of the stone.

Physical properties are more important if the limestone is used for aggregate or building stone. Strength and durability are of prime importance in the assessment of limestone for aggregate as well as other properties, such as porosity and water absorption.

The density of a rock is one of its most fundamental properties. It is principally influenced by the mineral composition and the amount of void space. Strength and hardness principally relate to density, porosity, moisture and homogeneity of a deposit. Frost susceptibility (in cold countries) and porosity are important properties in the assessment of a limestone for use as dimension stone. Physical property determination is also important in the assessment of limestone raw materials for filler and extenders applications. Rock strengths are also sometimes requires to make it is possible to dispense with test such as the friability test (Tamrock test) and impact hardness test in favour of some other form of tests; for example, in determining the crushing strength and Bond work index of the stone in the fine grinding analysis. The production of good quality lime depends partly on the physical properties of the raw materials. So measuring the reactivity of the lime, surface area, and the degree of decrepitating of the stone assesses the lime-burning performance of limestone. Particle size distribution, whiteness, surface area and oil adsorption are the most important physical characteristics of limestone powders for fillers in paint, plastics and papers.

2.4 LIMESTONE EVALUATION TECHNIQUES

The evaluation of limestone deposits for potential multipurpose applications needs to involve far more than a reconnaissance geological survey. It is necessary to determine the mineralogical, chemical, physical and mechanical properties of the stone and to compare these properties with raw material specifications for each end use. A sensible assessment of resources should, therefore, be based on a desk study, fieldwork and a laboratory assessment (Harrison, 1996).

2.4.1 Literature Survey

This is the review of available published and unpublished geological maps and documents, and information on depositional environment, structure and mineral occurrences. This pre-existing information may assist in resource identification and its current detailed investigation. It will further help in the investigation programme and exploitation planning of the resources in line with end-user and economic requirements.

2.4.2 Field Investigation

This programme generally encompasses two inter-independent factors of assessment activities, the geological survey and the economic assessment of the deposit.

2.4.3 Geological Survey

An assessment should begin with an initial field investigation involving field mapping, section measuring and sampling. Geological mapping aims to define the stratigraphical relationship and structure of the limestone formations, as well as determine lithologies. Further field investigations may include topographic and section surveys, sampling from exposures and drill core for subsequent laboratory analysis.

The choice of sampling techniques depends on the geology of deposit, the proposed end use of the limestone, and the availability of facilities and equipment. Certain geophysical techniques may be suitable for detailed investigations of limestone formation. Irregular structures such as underground drainage and cavity features can be determined by seismic survey. Electromagnetic and resistivity survey are particularly important in determining the distribution of poor quality rock in areas designated for quarry development. Down hole geophysical logging (particularly gamma ray) is useful in establish the clays and argillaceous units in limestone sequences and can enhance accurate borehole correlation. In-situ mechanical strength of the rock mass of limestone can be obtained with a handy Schmidt hammer (Bell, 1992), which is subjected to a range of factors such as the degree of weathering and fracturing, mineralogy and texture.

In many cases, the experienced geologist can identify dolomite in a limestone sequence by a weak acid solution, which usually exhibits a poor effervescence reaction, or by its appearance. A successful characterisation by staining techniques in distinguishing calcite and dolomite may also be applied in the field, although this requires experience and expertise.

2.4.4 Economic Assessment

Principle properties of mineral fillers and chemical-grade required by the end-user are varied in many facets. Each of these industries normally requires and indicates different kind of properties and purity. The evaluation of mineral deposits is essential by intended to provide fillers or chemical-grade products. A feasibility study is required of the mineral if it is to be classified as a mineral reserve, whether it is proved or probable, and profitable. The size of the deposit or reserve, quality and purity, transportation, amenities such as water and power requirements, marketing and competitiveness, costs of plant and building engineering, plant location, product and processing technology must all be investigated before any project is initiated.

A great variety of minerals can be used for particular industries depending on the market forces and performance or requirement of the end products. For evaluation of new deposits, especially for fillers, the type of feasibility study required would clearly have to include sufficient testing of the commercial parameters of likely commercial products to demonstrate that these products could be economically produced and would be acceptable to the user industries (Bristow, 1992). These tests should be applied on samples prepared to closely simulate commercial products. The most meaningful are commercial tests used by consuming industries for quality control, or in accordance with bodies such as Malaysian Standard (MS) British Standard Institute (BSI), or American Society for Testing and Materials (ASTM) standards. Requirement or specifications provided by the end user are the final decisive and conclude factors, and must be given an excessive consideration.

Some specifications are primarily economic rather than physical or chemical; for example, a low silica content in fluxstone is desirable, but the cost is an equally important factor. Generally, a silica content of less than 2% is desired. Unacceptable amounts of MgO could increase grinding costs, whereas Fe_2O_3 and SiO_2 are expensive to remove (Andrew and Vagt 1993).