February 2010 ISSN : 0974 - 7451 Volume 5 Issue 1

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 5(1), 2010 [68-72]

Studies of limestone samples sourced from the southern zone of Tamil Nadu, India

S.VijayaChitra[1], S.Thangadurai[2]*, R.Rajeswara Rao[3], T.S.Sankara Narayanan[4]

[1]Department of Geology and Mining, Govt. of Tamil Nadu, Guindy Chennai-600 032, (INDIA)

[2]Raja Doraisingam Government Arts College, Sivagangai-630 561, (INDIA)

[3]Department of Applied Geology, University of Madras, Chennai-600 025, (INDIA)

[4]National Metallurgical Laboratory, Government of India, Chennai-600 025, (INDIA)

E-mail : drstdurai@yahoo.co.in; drstdurai@gmail.com

Received: 4th January, 2010 ; Accepted: 14th January, 2010

ABSTRACT

Chemical analysis of 150 samples, which were locally sourced, was carried out using gravimetric, titrimetric, flame photometry and UV-visible spectroscopic methods. Based on the correlation study on the analytical results of some of the locally sourced samples were found to match with the specifications recommended for limestones for industrial applications. Limestone is chiefly made up of calcium carbonate ($CaCO_3$), its percentage in samples analyzed was found to range from 82.24±0.65 to 96.67±0.28 with a percentage mean value of 93.01±4.47. The results show that some of the limestone samples were found to meet some industrial raw materials specifications used in the cement, agriculture, poultry, paint, pharmaceutical, ceramics, glass, Silica bricks, metallurgical purification processes in the steel industry and some other filler applications.

KEYWORDS

Chemical analysis;
Spectroscopy;
Limestone;
Local source;
Industry.

INTRODUCTION

Limestones[1] are known to include organic, marl and chalk. It may also include layers of clay or sand which form the attractive flow bandings and the colors found in decorative marbles. Calcium carbonate ($CaCO_3$) is an abundant mineral comprising approximately 4% of the earth's crust. It is also a common sedimentary rock composed predominantly of carbonates of calcium and magnesium. These are the most voluminous of the non-siliciclastic sedimentary rocks. In the strict sense, limestones refer to sedimentary rocks composed of mineral calcite. As an inorganic mineral it is widely utilized both by humanity and nature. The $CaCO_3$ has received much attention owing to its wide application[2] in such industrial fields as paper, rubber, plastics, paint, in dentrifiers, deodordants, in face powder etc.

In addition, lime stones and dolomites are important reservoirs for oil and gas and are the hosts for important mineral deposits including Pb, Zn, Ag, and fluorite although most of the lime stones are similar in

chemical and mineralogical composition, the complex organic and chemical origins of carbonate sediments lead to a wide range of textures and fabrics finding wide application in industrial fields in the resulting lime stones.

The State of Tamil Nadu ranks seventh in India in terms of production of Limestone There are 12 major cement plants functioning in the State the total limestone reserves are about 1,473 million tones. The crystalline limestones of Tamil Nadu are perhaps the oldest 2660 million years of limestones in the world. The crystalline limestones in Tamil Nadu are found associated with quartzite, calc-silicate rocks and garnetiferous-silimanite-gneiss.

Researchers concisely described many complex relations between metamorphic rocks due to intense metamorphism coupled with intrusive activities this formation seen as heterogeneous assemblages of metamorphic facies in comparison with similar features observed in Greenland by the geologists. Small amounts of the arenaceous facies are represented by quartzite and garnetiferous gneiss. A number of impersistent bands are observed inter-banded with quartzites and garnetiferous gneisses.

The Pattamadai and Ambasamudram bands which form the southern most units occur within the khondalite rocks in Tirunelveli district and further extends into north-west south east direction into Kerala, the neighbourimg state of Tamil Nadu The charnokitic rocks occur inter banded with the meta sedimentary rocks in southern Tamil Nadu.

The chemical and physical analysis of limestone are increasingly important to the consumer as a means of evaluating the specific type/grade product required for optimum performance among the numerous uses in which these products are consumed owing to the wide range of these chemicals and physical characteristics many individual specification and tolerance have been developed for lime stones.

The Indian Standards Institution (ISI) has so far formulated a few specifications for limestone in various important industries. These specifications have been more useful to the small and medium scale producers of the country and have made possible the best utilization of the available indigenous resources.

EXPERIMENTAL

Apparatus

A flame emission spectrophotometer Systronics Model-125 was used to measure the emission intensities of the test samples in comparison with standard solutions.

A Systronics UV-visible spectrophotometer, Model 106 was used for the determination of iron, and titanium at 480nm, 410nm wavelengths respectively.

Procedure

One hundred and fifty (150) samples were collected from the Southern Zone of Tamil Nadu, India during the course of the investigation and these were later on analyzed in the laboratory and the chemical composition of the limestone were determined.

Chemical analysis[3] of selected limestone samples were carried out by conventional methods and the range of parameter determined were as follows Moisture, Loss on ignition (LOI), Silica (SiO_2), Oxides of Iron (Fe_2O_3), Titanium (TiO_2), Aluminium (Al_2O_3), Calcium (CaO), Magnesium (MgO), Sodium (Na_2O), Potassium (K_2O) and Total Carbonates. Gravimetric methods[4] were used for the determination of the proportions of insoluble matter, combined oxides in the samples.

Flame emission techniques were employed for the determination of the composition of Sodium (Na_2O) and Potassium (K_2O). A flame emission spectrophotometer Systronics Model-125 was used to measure the emission intensities of the test samples in comparison with standard solutions. A Systronics UV-visible spectrophotometer, Model 106 was used for the determination of iron, and titanium at 480nm, 410nm wavelengths respectively.

Jeffery et al.[5] described methods to carry out the determination of iron, thiocyanate method and for the determination of titanium, peroxide method. The absorbance of the test sample solutions was compared to those standard solutions similarly measured.

Percentage of carbonate in these limestone samples was roughly determined[6] during LOI analysis, but that was not enough to provide the actual carbonate / carbon dioxide content values of these samples

since alkali carbonates do not decompose on heating. As such a different method was employed to determine the actual percentage of carbonate composition in the limestone samples. The reaction of the carbonate samples with excess hydrochloric acid to produce CO_2 was utilized to ascertain the carbonate levels of the limestone samples.

Gas law calculations including correction for water vapour, gas solubility and Dalton's law of partial pressure were all used to determine[7] the correct volume of CO_2 evolved from each sample at laboratory conditions. The efficiency of this method was tested with analar (AR) grade $CaCO_3$.

RESULTS AND DISCUSSION

Limestone is a versatile material, which can support a wide range of chemical and other industries in the state. Any limestone with $CaCO_3$ in excess of 75% can find some industrial use or other and therefore warrants geological prospecting in order to make an assessment of reserves and quality and to determine the industrial possibilities. The usual compositional disparities between the samples imposed corresponding differences in their industrial and economic utilization. For such reasons, it is within the scope of this research work to assess the composition and possibly characterize the limestone samples obtained from the selected zones of Tamil Nadu, to assess their suitability and potential for industrial purposes.

Even though these samples were sourced from the same zone of Southern Tamil Nadu variations still existed due to the complex organic and chemical origins of carbonate sediments leading to a wide range of textures and fabrics finding wide application in industrial fields. Most of the limestone samples were found to meet some industrial raw material specifications used in the cement, agriculture (liming of soil and fish ponds), ceramics, glass, silica bricks, pharmaceutical, coal dust fire dampener, paint, poultry, cosmetics and other filler applications.

Samples collected from certain areas of Pillainatham village in Sankarankoil taluk, Tirunelveli district showed calcium content ranging from 45-55% to be of more industrial utility. Analytical results of samples collected from Ilankulam and Parapadi villages show the presence of low CaO content being prevalent in this particular area, the limestones are too impure to be of any value.

Analytical results of 25 samples collected from Kilakadavetti, Singikulam, Gangainadankulam villages of Nanguneri, Palayamkottai taluk show composition of significant industrial utility.

Samples collected from Venkatarangapuram of Ambasamudram taluk were found to contain about 45-53 % of CaO, suitable for wide range of application in industries. The analytical results of samples collected from Karisalapatti, Pillaikulam, Ganganarkulam and Pattankadu villages of Ambasamudram taluk of Tirunelveli district reveal the presence of CaO content in the range of 45-50 % being prevalent in this particular area.

Also the analytical results of samples collected from Iraipuvari village show the presence of CaO content in the range of 1-25 % being prevalent. In the northwestern part of Nanguneri taluk the limestones are too impure to be of any value.

As regard to the industrial utility of samples at Tuticorin district, based on the analytical report on samples collected in and around Pannamparai and Sathankulam villages of Tuticorin district, it may be concluded that the kankary limestones available in this area seems to be of cement grade[8,9]. They are found to contain only small amounts of CaO, Fe_2O_3 and MgO and high silica (SiO_2) contents. These limestones could be made useful for cement production by blending substantial quantity of high-grade limestone with high calcium and very low silica, (more than 95% $CaCO_3$ and less than 3% SiO_2) in suitable proportions.

It is imperative that many research and development programme should be undertaken for the proper utilization of existing deposits. Since many of the applications have either not developed or only established to a small extent, there is a tremendous scope for the establishment of a host of new industries emerging including the recently developed Ca-batteries industry. A careful search for the new deposits adopting modern methods of prospecting and exploration is essential. After fixing the new finds, they may be sorted

according to their suitability for the different industries; the recent technological innovations in cement manufacturing the world over have also provided ways and means of utilizing relatively impure varieties of limestone for cement production.

Analytical method suitable for the complex suite of phases contained within portland cement using online X-ray diffraction for quantitative phase analysis[10] have been recently developed. X-ray diffraction (XRD) analyzer capable of continuously monitoring phase abundances for use in process plant control have been developed The slags from blast furnace (iron making) and converter (steel making) after magnetic separation are mixed with limestone of six different compositions[11,12]. Blending 10% extra iron slag to a cement composed of 49% iron slag, 43% calcined lime, and 8% steel slag have been found to the compressive strength of concrete above standard values for ordinary portland cement. Effective ways of blending and enrichment techniques[13] would increase the utility value of the impure limestone deposits.

CONCLUSIONS

In this study, based on the analytical results the samples collected from certain areas of Pillainatham village in Sankarankoil taluk, Tirunelveli district showed calcium content ranging from 45-55% to be of more industrial utility.

The Samples collected from Venkatarangapuram of Ambasamudram taluk were found to contain about 45-53% of CaO, suitable for wide range of application in industries. Also the samples collected from Karisalapatti, Pillaikulam, Ganganarkulam and Pattankadu villages of Ambasamudram taluk of Tirunelveli district reveal the presence of CaO content in the range of 45-50% being prevalent in this particular area.

Kilakadavetti, Singikulam, Gangainadankulam villages of Nanguneri, Palayamkottai taluk show composition of significant industrial utility. The samples collected in and around Pannamparai and Sathankulam villages of Tuticorin district, based on the analytical report it is concluded that the kankary limestones are available in this area seems to be of cement grade.

The aforementioned area has only small amounts of CaO, Fe_2O_3 and MgO, but it contains high SiO_2 contents. These limestones could be made useful for cement production by blending substantial quantity of high-grade limestone with high CaO calcium and very low SiO_2 in suitable proportions.

A thorough research to explore the possibility of adopting developed techniques on certain relatively impure deposits would enhance the limestone utility level in industries to a greater extent. It has been proposed to do further study on the industrial utility of lime stone samples in certain other zones of Tamil Nadu. Further studies on the limestone samples sourced within Tamil Nadu when carried out should also be with a view to their meeting the specifications for pharmaceutical use and sugar refining.

ACKNOWLEDGEMENT

Authors express their sincere thanks to the Commissioner of Geology and Mining, Guindy, Chennai-600 032 for the encouragement throughout this work.

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