Mineral Resources of Jaisalmer

Abstract

Extensive deposits of high-grade limestone are located at various places in Jaisalmer district of Rajasthan. Laboratory scale experiments for producing precipitated calcium carbonate from the limestone of this area were carried out by the authors in the departmental laboratory. Milk of lime obtained after the calcinations of limestone and subsequent hydration, was subjected to carbonation at normal temperature and pressure conditions. The precipitated calcium carbonate was filtered, dried and weighted. The product obtained, analyzed 97.93% $CaCO_3$ and had dry brightness of 98%. The bulk density was 0.38 gms/cc and the weight percent recovery was 65%. The product was a mixture of about 60% calcite and 40% aragonite. The details of the work done are discussed in the paper.

Introduction

Precipitated calcium carbonate or precipitated chalk is a compound obtained by chemical precipitation of calcium carbonate and differs in physical properties from the $CaCO_3$ obtained by mechanical means i.e. by grinding calcite, marble, etc.

Calcium carbonate is the major constituent of limestone, calcite, aragonite, the latter two are naturally occurring crystalline forms of calcium carbonate, where as limestone is a rock of which calcium carbonate is the main constituent with impurities like SiO_2, Fe_2O_3, $A1_2O_3$, $MgCO_3$, etc.

The precipitated calcium carbonate is composed of either mainly of aragonite, or mainly of calcite or mixture of both, depending upon the precipitation conditions.

Different grades of precipitated calcium carbonate required for various industrial applications are given below:-

1. Light
2. Medium
3. Heavy
4. USP grade (Pharmaceutical)
5. As per IS specifications for rubber, paints, plastic, printing inks, paper, cosmetics, etc.
6. IP grade (Pharmaceuticals)

The product should have brightness and purity over 98%. The main impurities are SiO_2 and $MgCO_3$. Precipitated calcium carbonate or precipitated chalk is a fine, white, microcrystalline, odorless powder and is slightly soluble in water. Solubility increases in carbonated water due to the formation of water soluble $Ca(HCO_3)_2$. Between aragonite and calcite the solubility of the former is more than the latter. By suitably controlling the processing parameters, desired from of crystals can be obtained such as by passing CO_2 gas into a cold solution of milk of lime, calcite is obtained. If the CO_2 is passed in hot solution aragonite is obtained. Similarly strong solution will give calcite where as very dilute solution will give aragonite.

History

In the year 1898, precipitated calcium carbonate was first time used in paper industry and it was obtained from causticiser waste. Production of precipitated calcium carbonate from lime with kiln gases was started in 1913. The use in other industries like Pharmaceuticals, Paints, Rubber, etc. was developed by 1928.

Initially calcium carbonate was produced by the interaction of calcium chloride with sodium carbonate (1850). Gradually more economical process by direct carbonation of milk of lime for the production of PCC was developed.

Uses

Precipitated calcium carbonate finds many uses in various industries such as, filler in paper, paints, plastics, rubber, textiles, putties, adhesive, printing ink, etc. USP grades are used in dentifrices, cosmetics foods and Pharmaceuticals, etc.

Manufacturing Process

Following three manufacturing processes are usually employed for the production of precipitated calcium carbonate.

Calcium Chloride-Soda Ash by Product Process

In this process milk of lime is made to react with ammonium chloride solution as per following reaction.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2H_2O + 2NH_3$$

The ammonia gas is removed by heating. The remaining solution of $CaCl_2$ is treated with soda ash to give, calcium carbonate precipitate of very high purity.

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$$

This process is advantageous only when $CaCl_2$ liquor is obtained as by product such as in solvexy process and is feasible as an expansion unit of soda ash plant.

Lime Soda Causticisation by Product Process

When milk of lime is reacted with sodium carbonate, caustic soda is obtained along with calcium carbonate as by product.

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaOH$$

Lime Carbonation Process

As far as the production of lime and milk of lime is concerned the above-cited processes are common. In lime carbonation process the CO_2 obtained due to the decomposition of $CaCO_3$ is purified and used for the carbonation of milk of lime to obtained calcium carbonate as per following reactions:

heat

$$CaCO_3 \longrightarrow CaO + CO^2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + Co_2 \longrightarrow CaCO_3 + H_2O$$

The selection of the process depends upon, the technical feasibility (available of know how, engineering desing, plants and equipment and raw material and utilities, etc.) and economic feasibility (market, capital investment, return on capital, etc.). Among all the three processes discussed above the lime carbonation process is the most suitable and feasible process.

Experimental

To adjudge the suitability of high grade limestone occurring in Jaisalmer district of Rajasthan, Laboratory scale experiments were conducted to obtain precipitated calcium carbonate through lime carbonation route.

5 kgms sample was obtained from the samples of limestone of this area, received in the laboratory for chemical analyses. The sample varied in size from 3" to 6" (7.5 to 15 cm.) lumps and was yellowish in colour. The chemical analysis of the sample is given below: -

CaO	55.16%
MgO	0.60%
SiO_2	0.58%
R_2O_3 (Fe_2O_3 + $A1_2$ O_3)	0.40%
L.O.I.	43.04%

Sample was crushed to about 1" (2..5 cm.) size in a laboratory Jaw Crusher.

Calcinations

The carbonates of calcium and magnesium are stable at normal temperature but on heating at appropriate temperature depending upon the composition of the mineral, these are decomposed to give oxides of calcium and magnesium with the evolution of CO_2 gas. To have complete decomposition it is essential that material of uniform size is kept at properly controlled temperature for adequate time period. The decomposition occurs as per following chemical reaction:

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO^2$$

It is essential that for complete decomposition adequate heat is transferred to the centre of the lump to raise its temperature to decomposition point. This will also raise the partial pressure of carbon dioxide evolved above the total pressure of surroundings and will make CO_2 to move from inside to the outside of the lump. Temperature differential and partial pressure of carbon dioxide are the important factors for the complete decomposition of limestone.

Calcinations of crushed limestone under study were carried out in a laboratory muffle funance fitted with thermocouple and pyrometer. Normally decomposition of limestone occurs at 950^0 C. In this case the sample was calcined for three hours at 1000^0 C and allowed to remain in the furnace till the temperature was dropped down to about 200^0 C. This was done to achieve complete decomposition of limestone and also to prevent any attack on hot product by atmospheric moisture and CO_2. The material at 200^0 C was taken out and placed in desiccators for further cooling. The calcium oxide thus obtained was analyzed for SiO_2, R_2O_3, total CaO, available CaO, MgO and CO_2 the analysis is given as under:

Available CaO	93%
Dead burnt CaO	3.5%
CO_2	1.8%
SiO_2	0.5%
Fe_2O_3	0.13%
MgO	0.2%
$A1_2O_3$	0.07%

Hydration

Hydration is a process in which quick lime is treated with sufficient quantity of water to convert calcium oxide to calcium hydroxide as per following reaction.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Quick lime obtained was subjected to hydration by spraying controlled quantity of water. The hydrated product, which was almost dry, was passed through 85-mesh sieve. Under burned and dead burned material was rejected with the over sized material. Hydrated lime obtained was treated with excess of water to form milk of lime. The slurry was passed through 200-mesh sieve. Over sized material was rejected and mixed with the rejects obtained during hydration operation. Slurry passing through 200 mesh was diluted to a slurry density of 10% solids and subjected to carbonation.

Carbonation

A stream of carbon dioxide was passed into the dilute slurry obtained from slaking operation. Calcium hydroxide reacted with carbon dioxide to form calcium carbonate precipitate as per following reaction:

$$Ca(OH)_2 + Co_2 \longrightarrow CaCO_3 + H_2O$$

The end point of the complete conversion was noted when the pH of the process liquor reached around 7.

Precipitated calcium carbonate was filtered on a vacuum pan. Filter cake was dried, weighted and analyzed to determine the quality of calcium carbonate obtained. The results are given as under:

$CaCO_3$	97.93%
MgO	0.2%
Fe_2O_3	0.13%
$A1_2O_3$	0.07%
CO_2	43.5%
SiO_2 + Insoluble	0.5%
Bulk density	0.38% gms/cc.
Dry brightness	98%
Weight percent recovery	65%

Microscopic examination showed about 60% calcite and 40$ aragonite in the CC obtained at normal temperature and pressure conditions.

Quality of precipitated calcium carbonate obtained is greatly influenced by the slurry density, pressure temperature and pH employed during carbonation. The experiment was conducted under normal atmospheric pressure and temperature conditions.

Yellow Limestone (Marble) of Jaisalmer

Jaisalmer is famous for its beautifully carved havelies, palaces, forts and buildings made up of yellow coloured limestone [appears to be golden in colour]. It attracts the attention of people and justifies the name "Golden City of Rajasthan". Jaisalmer district has substantial limestone deposits, which are being used as marble, decorative stone and building stone since long back. The beautifully carved windows perforated Jallis, Jarokhas, wall facings, Chatries, Gumbach, Paroota, etc. attracts the attention of tourists. Thus Jaisalmer becomes an important tourist center for foreigners as well as Indian tourists.

Though there are large numbers of limestone occurrences in this district but two types of limestone deposits are being used as decorative stone and popurarly known in the marble trade are 'Jaisalmer yellow' and 'Supari' or 'Abur' marble. These decorative stones are dealt here with:

(i) Jaisalmer Yellow Marble

This limestone is mainly yellow coloured fine to medium grained almost horizontally placed belong to the Jaisalmer formation of town, within a radius of 10 kms covering Mool Sagar, Amer Sagar, Bara Bagh, Chundi, Bagta, Sipla, Jethwai, etc. villages.

There are three limestone horizons separated each other by thin beds of clay and calcareous sandstone. The thickness of each bed varies from 0.5 to 2.00 mts. The top most limestone bed is not suitable for use as marble as it is siliceous and fossiliferous in nature. The second and third bed is being excavated in form of blocks and khandas. The total depth of third limestone bed is generally 3 to 5 mts. This restricts the mining operation up to a depth of 5 to 6 mts. The mining is being done manually. At present mining for marble is restricted in Mool Sagar and Sipla area. The limestone excavated from Sipla and Chundi area are widely used for carving purposes.