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Sathiraju V Satyanarayana
Senior lecturer, Caledonian College of Engineering, Muscat, Oman.

Natiq Joodi
Assistant Professor, Caledonian College of Engineering, Muscat, Oman.

Shyam Agasthya
Lecturer, Caledonian College of Engineering, Muscat, Oman.

Shaik Feroz
Professor, Caledonian College of Engineering, Muscat, Oman.

Correspondence
Sathiraju V Satyanarayana
Senior lecturer, Caledonian College of Engineering, Muscat, Oman.

Food grade calcium carbonate from marble industry solid waste

Sathiraju V Satyanarayana, Natiq Joodi, Shyam Agasthya, Shaik Feroz

Abstract
Tajmahal (India), one of the Seven Wonders of the World, was built using marble stones. The white shiny marble stones are polished to use as flooring tails, wall tails, to make different statues and decorative items. Millions of tons of solid waste is being generated every year from marble industries. The solid waste from marble industry can be converted into food grade calcium carbonate. The solid waste is made into slurry with 30-40% solids. It is dissolved in dilute hydrochloric acid and precipitated as calcium carbonate using sodium carbonate. The product quality analysis matched with food grade calcium carbonate.

Keywords: Calcium carbonate, Food grade, marble, Slurry, solid waste

Introduction
The solid waste from marble industry contains 80-90% $CaCO_3$.It contains different types of impurities like iron, magnesium, sodium and other metals and non-metal ions. Calcium carbonate is being used in paper industry, paint industry, plastic industry, ink, cosmetics, food and pharmaceutical industries. An average paper mill uses about 20–100 thousand tons of precipitated calcium carbonate per year (Sebastian, 2005) [2]. Calcium carbonate can be prepared by mixing hydrated lime with sodium carbonate. A series of batch reactions were performed keeping lime as limiting reactant in the first stage for each batch. In second stage, sodium carbonate was the limiting reactant by having excess lime (Islam, 2008) [3]. The impurities in marble stone varies from mine to mine. To increase the purity of calcium carbonate, residual impurities are to be eliminated. Several factors account for low chemical conversions (Michel, 1988) [1].

Methodology
The marble industry is generating 30-40 tons of solid waste per day. The solid waste contains nearly 75-80% calcium carbonate, 15- 20% moisture and 5%.other inorganic impurities like metal oxides, organic impurities like anionic poly electrolyte and carbon from diamond cutters.
Food grade calcium carbonate production process consists of three stages.

Stage-1
Solid waste solution preparation
In a stainless steel tank required quantity of water is added to the solid waste and made in to slurry with 25-30% solids.
In another HDPE tank 15% dilute hydrochloric acid is prepared by mixing concentrated HCl with water.
In a stainless steel tank solid waste slurry and dilute hydrochloric acid are mixed slowly with constant stirring till the slurry dissolved completely. The insoluble calcium carbonate is brought in to soluble calcium chloride form
Calcium chloride solution is passed through a sand bed to remove all suspended particles. The sand bed out let solution collected separately.

Stage-2

Preparation of Sodium Carbonate Solution:

In a stainless steel tank 15% sodium carbonate solution is prepared. For 1000 liters of water 150 kg of sodium carbonate is added and mixed thoroughly till it is dissolved completely.

Stage-3

Preparation of Calcium Carbonate

Calcium chloride solution and sodium carbonate solution are pumped (or by gravity) in to a stainless steel tank. The two solutions are continuously stirred to precipitate calcium carbonate.

The insoluble calcium carbonate is filtered and washed using fresh water to get food grade calcium carbonate. The material is dried at 50 ^{0}C for 24 hours (Abdullah, 2013) [4] to get 98% calcium carbonate.

The product calcium carbonate samples were analyzed using "Inductively Coupled Plasma Spectrophotometer" (I.C.P.S).

Results

Food grade calcium carbonate samples from five batches are analyzed for purity, potassium, magnesium, lithium, moisture and other heavy metals. The results are shown in Table 1.

Table 1: Percentage of purity of calcium carbonate in different samples.

S. No	% $CaCO_3$	K %	Mg %	Li mg/l	Moisture %
Sample-1	97.3	0.27	0.35	0.05	0.48
Sample-2	96.6	0.36	0.42	0.06	0.69
Sample-3	96.1	0.33	0.46	0.04	0.72
Sample-4	97.8	0.29	0.38	0.03	0.46
Sample-5	97.2	0.31	0.44	0.07	0.48

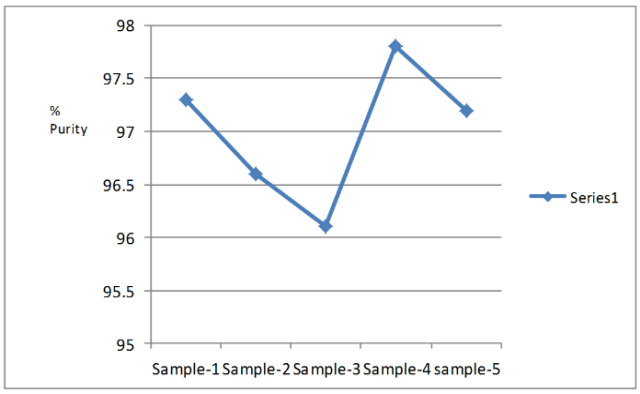

Fig 1: Purity of calcium carbonate

The European Food Safety Authority (EFSA, 2011) [5] specifications for food grade calcium carbonate are shown in Table-2.

Table 2: Food grade Calcium carbonate specifications

S. No	Parameter	Maximum permissible limit
1	Purity	≥ 98%
2	Loss on drying at 200 ^{0}C for 4 hours	≤ 2.0%
3	Magnesium and alkali metals	< 1.5%
4	Fluoride	≤ 5 mg/Kg
5	Arsenic	≤ 3 mg/kg
6	Lead	≤1omg/Kg
7	Cadmium	≤ 1mg/Kg

Discussions

Samples 1, 4 and 5 are very close to food grade calcium carbonate. The samples have more than 97% purity. Potassium values varied from 0.27% to 0.36%. Magnesium values varied from 0.35% to 0.46% and moisture values varied from 0.46% to 0.72%.

Other metals like iron, copper, cadmium, chromium, aluminum, boron, barium, manganese were not detectable. They have shown negative values.

The chemical reaction to dissolve the solid waste is as given below.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + HCO_3^- + H^+$$

For 100kg of solid waste 73 kg of hydrochloric acid is required. It will give 110 kg of calcium chloride on dry basis. The chemical reaction to produce calcium carbonate is as given below.

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

111 Kg of calcium chloride is mixed with 106 Kg of sodium carbonate to get 100 Kg of calcium carbonate on dry basis.

Conclusion

The solid waste has been converted in to food grade calcium carbonate. It is a value added product from solid waste. Hence, no solid waste is generated from the marble industry. Waste water can be treated and can be reused in the process. This is a green technology for marble industry.

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