

# Demonstration of Capability of Low-Cost Calcium Carbonate to Restore Ph Levels of Sea for Protection of Marine Animals Post Oil Spills Due to Ship Grounding / Accidents as Part of Salvage Operations

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**Abstract:** *When a sea going vessel is grounded, the most dangerous effect of MARPOL is due to spillage of this fuel/oil which is discharged into the sea in enormous quantities and may also contain other acidic impurities. The effects of oil spillage include damage to marine life such as fishes, corals and sea shells. The ph of sea water generally varies between 8 to 9 and the same is regarded as congenial for biological existence of certain forms of marine life. Oil spills from ships containing fuels/oils cause acidification of sea water and result in lowering of ph of the affected area of sea water thereby causing death to marine life. Used CO<sub>2</sub> absorbent which is chemically high-grade Calcium Carbonate in granular form (size <5 mm) can be used to neutralize and restore the ph of sea water contaminated through oil spill. The same was experimentally verified.*

**Keywords:** Calcium Carbonate, MARPOL, Ocean Acidification, Ph-restoration, Trials

## 1. Introduction

### Ocean Acidification

A pH unit is a measure of acidity ranging from 0-14. The lower the value, the higher the acidity of the environment. A shift in pH to a lower value reflects an increase in acidity. When carbon dioxide (CO<sub>2</sub>) is absorbed by seawater, chemical reactions occur that reduce seawater pH, carbonate ion concentration, and saturation states of biologically important calcium carbonate minerals. These chemical reactions are termed "ocean acidification" or "OA" for short. Calcium carbonate minerals are the building blocks for the skeletons and shells of many marine organisms. In areas where most life now congregates in the ocean, the seawater is supersaturated with respect to calcium carbonate minerals. This means there are abundant building blocks for calcifying organisms to build their skeletons and shells. However, continued ocean acidification is causing many parts of the ocean to become undersaturated with these minerals, which is likely to affect the ability of some organisms to produce and maintain their shells.

## 2. Literature Survey

- **General Causes of OA:** Since the beginning of the Industrial Revolution, the pH of surface ocean waters has fallen by 0.1 pH units. Since the pH scale, like the Richter scale, is logarithmic, this change represents approximately a 30 percent increase in acidity. Future predictions indicate that the oceans will continue to absorb carbon dioxide, further increasing ocean acidity. Estimates of future carbon dioxide levels, based on business as usual emission scenarios, indicate that by the end of this century the surface waters of the ocean could have acidity levels nearly 150 percent higher, resulting in

a pH that the oceans haven't experienced for more than 20 million years.

- **Accidental Causes of Localised OA:** It is a known fact that pH of diesel fuels which are used for marine propulsion varies between ranges of 5.5 to 8. When a vessel is grounded, the most dangerous effect of MARPOL is due to spillage of this fuel/oil which is discharged into the sea in enormous quantities and may also contain other acidic impurities. The effects of oil spillage include damage to marine life such as fishes, corals and sea shells. The pH of sea water varies between 8 to 9 and is regarded as congenial for biological existence of marine life. Oil spills from ships containing fuels/oils cause acidification of sea water and result in lowering of pH of the affected area of sea water thereby causing death to marine life.
- **Biological Impact of OA:** Ocean acidification is expected to impact ocean species to varying degrees. Photosynthetic algae and seagrasses may benefit from higher CO<sub>2</sub> conditions in the ocean, as they require CO<sub>2</sub> to live just like plants on land. On the other hand, studies have shown that lower environmental calcium carbonate saturation states can have a dramatic effect on some calcifying species, including oysters, clams, sea urchins, shallow water corals, deep sea corals, and calcareous plankton. Today, more than a billion people worldwide rely on food from the ocean as their primary source of protein. Thus, both jobs and food security in the world depend on the fish and shellfish in our oceans.

## 3. Methods and Approach

### Properties of Calcium Carbonate

Calcium carbonate is a chemical compound with the formula CaCO<sub>3</sub>. It is a common substance found in rocks as

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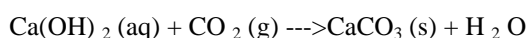
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the minerals calcite and aragonite (most notably as limestone, which is a type of sedimentary rock consisting mainly of calcite) and is the main component of pearls and the shells of marine organisms, snails, and eggs. Calcium carbonate is the active ingredient in agricultural lime and is created when calcium ions in hard water react with carbonate ions to create limescale. It is medicinally used as a calcium supplement or as an antacid, but excessive consumption can be hazardous and cause poor digestion.

#### Sources of Supply for Porous Granular Calcium Carbonate

Although it is clear that Calcium Carbonate occurs naturally, a better tested and granulated form of the same is available in abundance otherwise also. CO<sub>2</sub> absorbents are primarily manufactured from Calcium Hydroxide and are the key sources of calcium carbonate. This is evident from the reaction in which CO<sub>2</sub> scrubbers eliminate CO<sub>2</sub> from given air samples as follows: -



The calcium carbonate so produced is a disposal waste product when the endurance of the scrubber canisters is exhausted and is generally dumped as a waste. This disposal waste is produced from the following known scrubbers-based systems: -

- Scrubber systems of commercial Recompression Chambers
- Scrubber canisters of Commercialized Nitrox Diving Sets
- Scrubbers used in Medical Filtration Systems
- Industrial Grade CO<sub>2</sub> absorbent scrubber Filtration systems

## 4. Results and Discussion

### 4.1 Proposal

It is proposed that used CO<sub>2</sub> absorbent which is chemically high-grade Calcium Carbonate in granular form (size <5 mm) can be used to neutralize and restore the pH of sea water contaminated through oil spill. This is to be carried out in conjunction with suction sweeping of oil on the sea surface which effects the dissolved oxygen levels of sea water directly. Other perceived benefit of calcium carbonate is that it assists in regrowth of damaged corals/shells as their body structure's main constituent is itself calcium carbonate and there are practically no perceived side effects of using calcium carbonate in sea water.

### 4.2 Report of Trials and Testing

Trials and testing of the abovementioned methodology for pH restoration of contaminated sea water was carried out in three phases as follows:-

- Phase I:** Phase I was conducted at Laboratory in a stepwise manner carrying out confirmatory trials at least three times each as follows:-

Step	Sample	ph Value	Remarks
(i)	Pure Sea water	8.6	Alkaline
(ii)	50 ml sea water contaminated with 100 ml fuel oil	7.5	ph reduced by 1.1 unit
(iii)	50 ml sea water contaminated with 100 ml fuel oil mixed with 5 gms of CaCO <sub>3</sub>	8.2	ph value shifted closer towards original value

- Phase II:** Phase II was conducted in a similar manner as para 1(a) at a location near a local beach of Wellington island in Kochi as follows: -

Step	Sample	ph Value	Remarks
(i)	Pure Sea water	9	Alkaline
(ii)	Contaminated sample from beach by putting one liter of fuel oil into the sea	8	ph reduced by one unit
(iii)	Mixing above contaminated sample with 2gms of CaCO <sub>3</sub>	8.9	ph value restored to approximately the original value

- Phase III:** Phase III of the trials was conducted at Ernakulum Channel during low water near drying heights as follows:

Step	Sample	ph Value	Remarks
(i)	Pure Sea water	8.6	Alkaline
(ii)	Contaminated sample from Ernakulum Channel	7.9	ph reduced
(iii)	Sample from channel post mixing of Calcium Carbonate	8.5	ph value restored to approximately the original value
(iv)	Contaminated sample from Ernakulum Channel taken after 3 hours without dispersing Calcium Carbonate	8	ph reduced
(v)	Contaminated sample from Ernakulum Channel taken after 3 hours post dispersing Calcium Carbonate	8.5	ph restored

## 5. Conclusion and Future Scope

It is concluded from above trials that adding used CO<sub>2</sub> absorbent (high grade calcium carbonate, purity >90%) to oil fuel contaminated sea water can catalyse the process of restoration of pH balance to normal limits which naturally takes longer durations thereby reducing mortality rate of marine organisms. The quantity of calcium carbonate required is approximately of the ratio of 1:1000 (eg 1000T of oil spillage will require about 1T of absorbent). This ratio is a rough estimate as obtained through testing under available trial conditions. Actual amount of absorbent has to be calculated based on pH specifics in the area under application.

## References

- Refer to <https://www.pmel.noaa.gov/co2/story/What+is+Ocean+Acidification%3F>
- Refer to <https://www.government-fleet.com/157049>
- Refer to <https://www.pmel.noaa.gov/co2/story>

## Author Profile



I, Lt Cdr **Mayank Sharma**, is presently serving in Indian Navy. I have actively researched in various areas such as hyperbaric procedures for drug administration, methods to prevent soil erosion, innovative techniques to remove toxic gases from confined spaces, methods to reduce CO<sub>2</sub> pollutant from vehicle exhausts and a variety of diverse fields of research. I have an intuitive insight and believe that all new work and invention needs to be started without any preconceived thoughts and hence I start my research with a completely new approach without any previous references and try to achieve the goal of the research as perceived for the better good of the human community.