

A Note on Remobilization of Heavy Metals from Beachrocks to Coastal Water as Consequence of Sea Water Acidification

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Abstract

Sediments are considered as reservoirs of metals, many studies have shown the ability of beachrocks "rocks that form on the beaches" for trapping metals during the process of formation and cementation. The beachrocks are chemically composed primarily of calcium carbonate "CaCO₃" which easily allows the weathering of rocks and releasing metals trapped before "washing" as a result of acidity. In this note we highlight the probable remobilization of metals from beachrocks to coastal waters by leaching due to rising acidity of seawater.

Key Words: heavy metals; sea water; beachrocks; pH variability; calcium carbonate; pollution

1. Introduction

Industrial and urban activities in coastal areas introduce significant quantities of pollutants in the marine environment, causing permanent disruption of marine systems and therefore environmental and ecological degradation. Contamination of seawater by heavy metals is due to industrial effluents and land saturation by solid waste ([1], [2]). Coastal and estuarine sediments are considered as reservoirs or wells of many chemical pollutants, particularly heavy metals. Metal contamination of sediments is a danger for water, inhabiting species and human health ([3], [4]). According to the geological dictionary [5], beach sandstones or "beachrocks" are friable sandstone with limestone cement, which form on some sedimentation carbonate beaches. By extension, the term is used even when the elements of rock are largely or even solely composed of limestone debris (figure 1 and 2). What is known in coastal morphology as the beachrock; a beach sediment consolidated by calcareous cement. This intertidal consolidation can be a current or former phenomenon [6].



Figure 1. Beachrock Collected Along the Arzew gulf (Algeria)

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Figure 2. A: Beach Rock along the Beach of Coral Bay. B: Detail of a Beach Rock Showing the Incorporation of Shells and Fragments of Sandstone (Arrow), Australia, [7]

Sandstone beaches during their diagenesis and outside the formation phenomenon can trap heavy metals ([8],[9]), but these rocks are subjected to different climatic and hydrodynamic phenomena. This note highlight the contribution of chemical conditions "pH raising" on alteration of beachrocks and the releasing of heavy metals previously trapped.

2. Beachrocks Formation and Chemical Composition

There are a number of theories regarding the process of beach sand cementation. Different mechanisms of cementation appear to be responsible at different localities. The primary mechanisms proposed for the origin of beachrock cements are as follows ([10]):

- Physicochemical precipitation of high-Mg calcite and aragonite from seawater as a result of high temperatures, CaCO_3 supersaturation, and/or
- Physicochemical precipitation of low-Mg calcite and aragonite by mixing of meteoric and fresh ground water with seawater;
- Physicochemical precipitation of high-Mg calcite and aragonite by degassing of CO_2 from beach sediment pore water;
- Precipitation of micritic calcium carbonate as a byproduct of microbiological activity.

2.1. Heavy Metal Presence in Beachrocks

According to different researchs; beachrocks are trapping heavy metals during formation, table 01 shows mercury presences in some beachrocks over the world.

Table 1. Mercury Presence in Beachrocks from Some World Regions

Area	Mean Hg ($\mu\text{g.g}^{-1}$)	Mean CaCO_3 (%)	References
Arzew Gulf, Algeria	2.4	61.11	[9]
Gulf of Mannar, India	0.174	79.35	[8]
Southern California Bight	0.05	–	[11]
Taranto Gulf	0.12	–	[1]

3. Sea Water Acidification

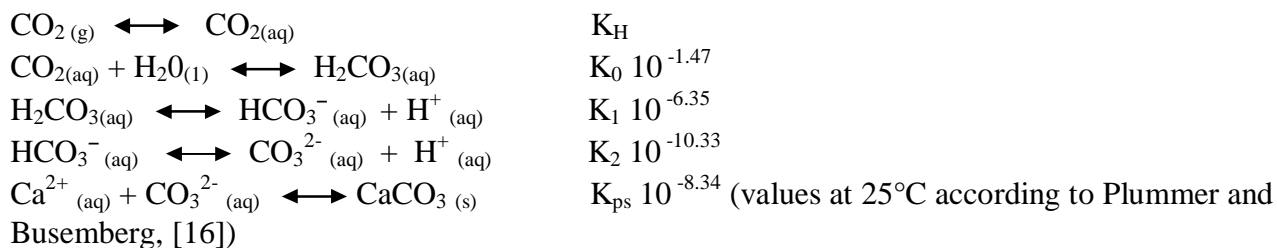
Sea water acidification is due to many factors and sources. PH variability is affecting marine health ecosystem as described in different studies.

The major driver of surface ocean pH change is the addition or removal of CO₂ by physical or biological activities. Photoautotrophic CO₂ depletion can cause significant diel pH oscillation with the lowest pH occurring during the night when CO₂ is released by respiration, while the highest values occur during the afternoon when photosynthesis removes CO₂. This diurnal oscillation is superimposed upon seasonal variations in pH, with lowest mean pH occurring in winter and highest in summer, due to changes in water temperature, the gross photosynthesis and respiration of the community [12]. Excessive biological production of organic matter (OM) in coastal ocean surface waters induced by human inputs of nutrients (that is, eutrophication) and the subsequent development of hypoxia ([O₂] < 62.5 μM) in subpycnocline waters (that is, the lower part of a stratified water column) due to respiration of the sinking OM have been reported with increasing frequency.

This process has received global attention because of the negative impact of eutrophication and hypoxic events on coastal ecosystems. The same respiratory processes, however, also release carbon dioxide (CO₂), lowering the pH (that is, increasing acidity) of subsurface waters in these regions [13]. Ocean acidification, resulting from dissolution of atmospheric anthropogenic CO₂ in oceanic waters, represents an additional emerging global threat to the health of marine ecosystems. Coastal ocean waters undergo natural pH fluctuations on daily, seasonal, and even inter-annual scales; however, the atmospheric CO₂ increase has also caused long-term increases in sea surface CO₂ concentration, resulting in decreases in pH. Such a trend is predicted to alter patterns of biogenic carbonate formation and may also significantly affect other ocean biogeochemical cycles [13]. Also pollution of sea water due to anthropogenic activities contributes significantly to chemical water parameters change (pH) [14]. Recent studies concluded generally that the decrease in calcification at high-CO₂ levels was due to decreased pH values [15].

4. Chemical Reaction

The calcium-carbon system can be represented by the following reactions ([20]):

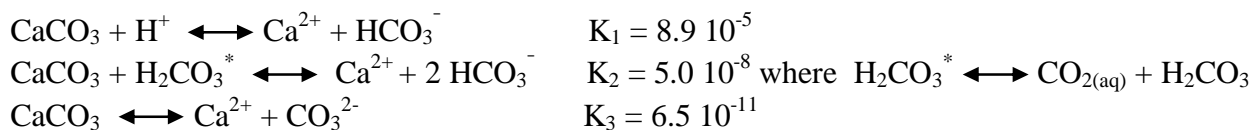


The total amount of an element is invariant and equal to the sum of all the chemical species containing. This relationship is the equation of conservation of matter.

4.1. Beachrocks Dissolution

We consider Beachrocks as carbonate rocks due to the high presence of CaCO₃, so the dissolution is influenced by many parameters such as pH, thermodynamics conditions, temperature, salinity, presence of inhibitors (Mg²⁺, HPO₄²⁻), surface morphology ([17], [18], [19], [20], [21], [22], [23], [24], [25]). In our study we focus on pH influence only.

Reactions that may be involved during the dissolution of CaCO₃ are [19]:



4.2. Kinetics of Dissolution

Figure 3 shows that for the usual pH of seawater, the HCO_3^- ion is predominant on the carbonate ion and $\text{CO}_2(\text{aq})$, figure 4 shows summary of kinetics dissolution of CaCO_3 according to temperature and pH.

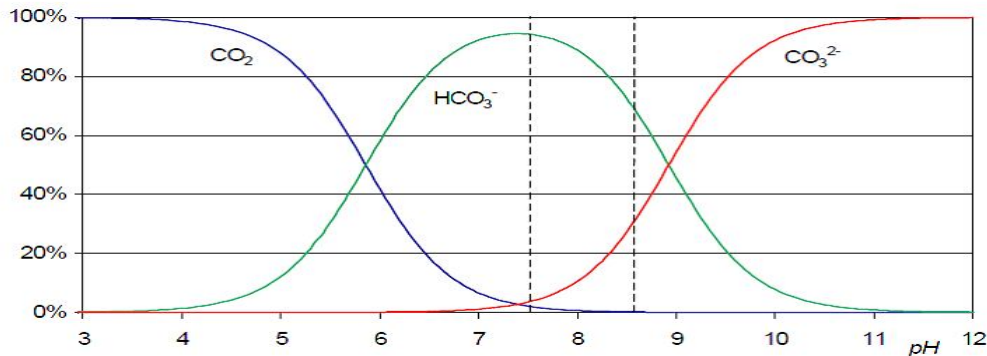


Figure 3: Variation Depending on the Ph Of $[\text{CO}_2]/\text{TC}$, $[\text{HCO}_3^-]/\text{TC}$, $[\text{CO}_3^{2-}]/\text{TC}$, in Water Of 35 Salinity and at 25°C

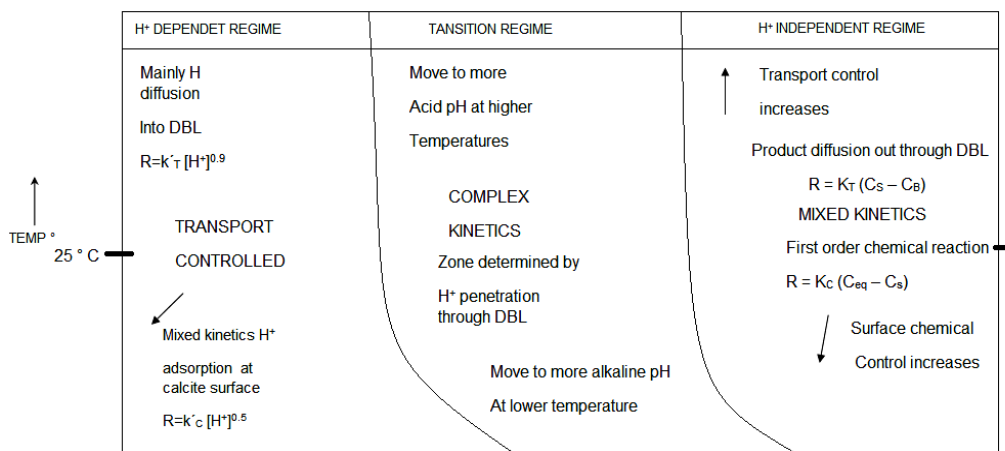


Figure 4: Kinetics Dissolution Regimes According to Ph and Temperatures [18]

5. Discussion and Conclusion

Calcification in a marine environment is highly related to the acidity of the latter, it is clear that the increasing acidity disrupts the balance by slowing the calcification which leads us to conclude that the formation of beachrocks is also slowed and maybe even canceled.

If we consider that the degree and rate of rock alteration is in relation with rock's surface, it may be said that beachrocks are increasingly subject to dissolution because the cementation is not continuous; this is due to pH decrease which does not allow rocks cementation by maintaining limestone dissolved. Therefore sea water pH decreasing due to CO_2 reabsorption by ocean, eutrophication and human activities releasing acid effluents contribute significantly to beachrocks dissolution and even sedimentary rocks. Alteration allows liberating trapped heavy metals and contamination of water, marine fauna and flora, and even human health via the chain food.

As a conclusion we can say that the acidification of sea water can cause heavy metals releasing from sedimentary rocks and therefore pollution of coastal waters affecting marine ecosystem health and even human health. This is another indirect consequence of CO₂ increase due to human activity.

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