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GEOCHEMICAL MODELLING FOR SEA-BED MINERAL FORMATION—A PROPOSAL

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Basic informations on manganese nodule have been presented to build up a theory of nodule nucleation on sea floor. Two alternative designs of experimental set-up for nucleation of nodule in laboratory have been suggested. It is proposed that a set of ideal geochemical parameters for formation of nodules may be collected from various sources and use them as guides for prospecting of potential fields.

Key Words : Mn-nodules; Pelagic; Geochemical; Simulation; Leaching

INTRODUCTION

PELAGIC sediments contain an average of about ten times the amounts of the industrially important metals as do the igneous rocks on land.[1] Besides having high Clarke values for some of these metals they also have ideal geochemical environments for concentration and intense focussing of certain elements by geological processes. Therefore, formation of manganese nodules on the ocean floor may be considered to be a common and natural geological phenomenon.

Although occurrences of manganese nodule in deep sea floor was first reported more than a century ago by Challenger expedition, only in the late sixties aecelerated investigation started and presently, the sea-bed nodule is considered to have potential economic value. The importance of manganese nodules is mainly due to their polymetallic composition which makes them economically viable. Unlike any other mineral resources, they are also replenishable in historic time. Several other factors like, nature of their distribution, persistence of grade, mining methodology and allied technological problems in regard to their exploitation are also considered favourable for their economic viability.

BASIC INFORMATION

Although considerable amount of field data have been collected by a few international parties operating in nodule harvesting, the same have not been made public for obvious reasons. However, published data are available in regard to the nature of distribution, morphological characters, mineralogical association, chemistry as well as mechanism and mode of formation of nodules on ocean bed. Some of these, relevant to the present problem are stated as follows :—

1. Although manganese nodules are abundant throughout the ocean, they are more common in certain geomorphic environments. Based on their depositional environments, occurrences of nodules have been classified as deposits of ocean sea mounts, plateaus, active mid-oceanic ridges, inactive ridges, continental border lands, marginal topographic elevations, deep ocean floor types etc.[2] Their nucleation is favoured, in sites of low rate of sedimentation and in the presence of strong oceanic currents. Nucleation is favoured in the sediment-water interface.

2. Density of distribution of the nodules on sea floor varies from 75 per cent or more to zero coverage. However, in actual practice the average density of distribution has been reported to vary from 0.2 to 2.5g/cm^2.[3]

3. Size of the nodule varies from 1mm (micronodule) to hundreds of cm, but generally in the range of 1 to 25cm with an average of 5cm. The shape is normally spherical with smooth or grannular surface and specific gravity ranges from 2 to 3 depending on contents and porosity.

4. Internal structure is concentrically banded, indicative of colloidal deposition. Filling of diagenetic cracks and presence of single or multiple nuclei at the core are common.

5. The principal mineral constituents are 7Å manganite (birenessite), 10Å manganite (todorokite), δ–MnO_2 and goethite with other accessory minerals like zeolite, clays and silica.

6. Chemically, the nodule composition may be predominantly manganiferous, calcareous or silicious, and in case of the former, it contains, besides iron, considerable amounts of Co, Ni, Cu, Zn, Pb, V etc. to the extent of 2 to 3 per cent. Compositional difference in terms of trace metal contents have been recognised in various nodule fields. For examples, sea-mount nodules are high in Co, continental border line nodules have high Mn/Fe ratio and the abyssal nodules are rich in Cu.[4] Even in a single nodule, the portion above the sediment surface has been found to be relatively richer in Fe, Co and Pb and poorer in Cu, Ni, Mo, Zn and Mn, obviously due to postdepositional leaching indicating undersaturation of sea floor water for the leached constituents.[5]

7. Nodules are considered to have formed on sea floor by processes such as simple precipitation from sea water, deposited from hydrothermal solution. ocean floor weathering of volcanic rocks or by diagenesis. Manganese nodules have also been nucleated by Raab and Meylan[5] in laboratory within a short span of a few weeks.

Based on the above basic information, gathered from field and laboratory studies, and from theoretical approach regarding stability of iron and manganese in aqueous environments,[6] it is possible to construct a geochemical model for an idealised nodule field. The collected data may be appraised to recognise a set of ideal parameters of nodule nucleation and can be profitably used as guidelines or indicators in exploration of new nodule deposits (Table I).

TABLE I

Flow sheet for geochemical modelling

1. DATA COLLECTION

Field Data	: Geochemical parameters recorded in known nodule fields : Eh-*p*H, salinity, P-T conditions, current characteristics, photometry, basement topography and materials.
Laboratory Data	: Mineralogy, texture, structure, crystal chemistry, state of major trace elements in the matrix: physico-chemical environment inferred therefrom.
Theoretical Data	: Stability of Fe-Mn compounds in presence of trace metals at various physicochemical environments.
Experimental Data	: Laboratory simulation of natural environment for nodule nucleation and data derived therefrom.

2. DATA PROCESSING AND APPRAISAL

Compilation and processing of all data on geochemical environments of nodule nucleation and appraisal of most ideal geochemical environments for nodule nucleation. Development of a set of optimum geochemical parameters for nodule exploration.

3. DATA APPLICATION

Application of the set of derived parameters as exploration aids.

EXPERIMENTAL SIMULATION

One of the sources of such data proposed above being experimentally simulated systems, the hypothesis behind the mode of formation backing such experimental set-up needs to be examined. Although the sources of manganese and associated elements in the nodules could be various, the proposed experiment envisages nodule nucleation at the sediment-water interface by solution derived from the circulating sea water beneath the ocean floor. Such a mechanism of convection of sea water is widely accepted by geologists.[7] Percolating sea water heated up due to geothermal gradient, is an ideal scavenger of many metals from the underlying rock and ultimately brings them to the ocean floor surface. That a considerable amount of manganese can be derived to reach the ocean floor and iron is left behind has been very well illustrated by Bonatti[8] from an electronprobe analysis of core and rea m of volcanicglass reacted with sea water (Table II). The process of spillitization so extensive in ocean floor, can very well release manganese for nodule nucleation. Even a fraction of the manganese released by alteration of the oceanic rock by reaction with the aggressive sea water will be enough for the formation of a rich nodule field. A rough estimation shows that, mobilization of half the manganese content of the ocean floor basalt by such alteration, upto a depth of 100cm, will eventually give rise to 60 nodules, 100g each, with 50 per cent MnO_2, spread over one sq. meter ocean floor (Fig. 1). Even if only a fraction of

TABLE II

*Electronprobe analysis of volcanic glass reacted with sea water**

	Core	Altered Rim		Average %	
		1	2	Loss	Gain
SiO_2	50.3	42.4	45.4	16	—
Al_2O_3	14.7	13.1	11.6	17	
FeO	9.9	16.9	18.6		80
CaO	11.6	5.3	7.0	46	
MgO	7.8	3.2	3.7	44	
K_2O	0.1	2.7	3.4		3000
Na_2O	3.1	1.5	2.2	60	
MnO	0.2	0.1	0.1	50	(Released for Mn-Nodule)

Basaltic Glass + Sea water → Zeolite (Phillipsite) + Fe Smectite + $Fe(OH)_3$ + MnO_2 (For nodule)

*After Bonatti (1970)

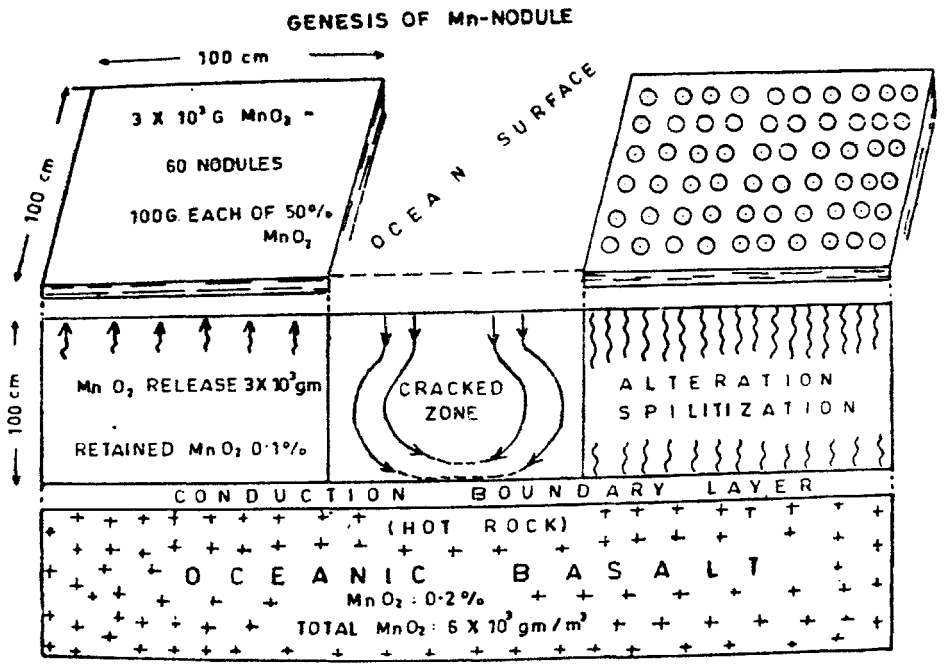

FIG 1 A hypothetical model for nodule genesis with rock leachate derived by interaction of convecting sea water beneath ocean floor.

the estimate is actually materialised for mobilization and precipitation of the metal, a large concentration of nodule can still be obtained on the ocean floor, because

the actual depth of circulation of water and alteration of the rock beneath, normally extends beyond 100cm.

With this hypothesis in the background that, nodules nucleate at the sediment-water interface by slow percolation of solution vertically across an illite rich oceanic floor, after having derived from leaching of oceanic basalt, the experimental set-up in Fig. 2 has been designed. It consists of a leaching chamber, virtually an autoclave, where rocks of desired composition and suitable mesh can be "cooked" under controlled environments and the leachate collected at the base of the autoclave. The leachate is introduced into the nucleating chamber from below, through a semipermeable porcelain plate over which a layer of illitic clay, calcareous/silicious ooze or red-mud has been laid. The solution seeping through this layer of soft sediment, is expected to nucleate in the sediment-water interface, where seeds of calcite, zeolite, silica, volcanic glass or even Mn-ore minerals could be hung for initiation of nucleation. The chemical parameters of the water in the nucleating chamber could be varied as desired. A number of runs can be operated and all variables in the leaching as well as nucleating chamber could be noted with results obtained.

An alternative design of the experimental set-up has also been made (personal communication)[9] and the same is show n in Fig. 3. It consists of a tall cylindrical chamber into which a module capable of recording various geochemical parameters at various levels can be introduced. The chamber is cooled by an outer annular compartment carrying ice cold water, so that a temperature gradient is vertically maintained in the nucleating chamber. An artificial solution equivalent to ocean water or rock leachate at elevated temperature, with known constituents

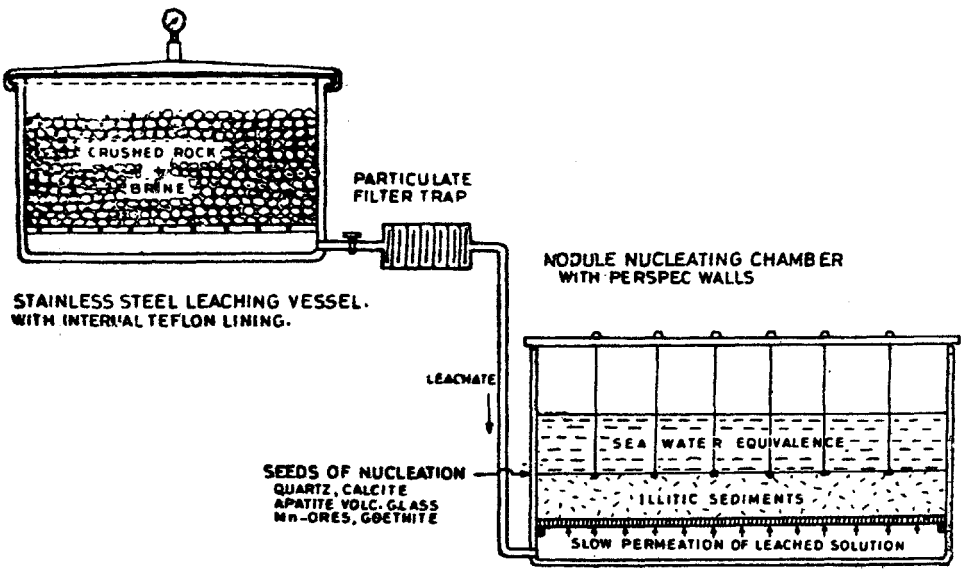

FIG 2 Design of an experimental set-up for Mn-nodule nucleation in the laboratory.

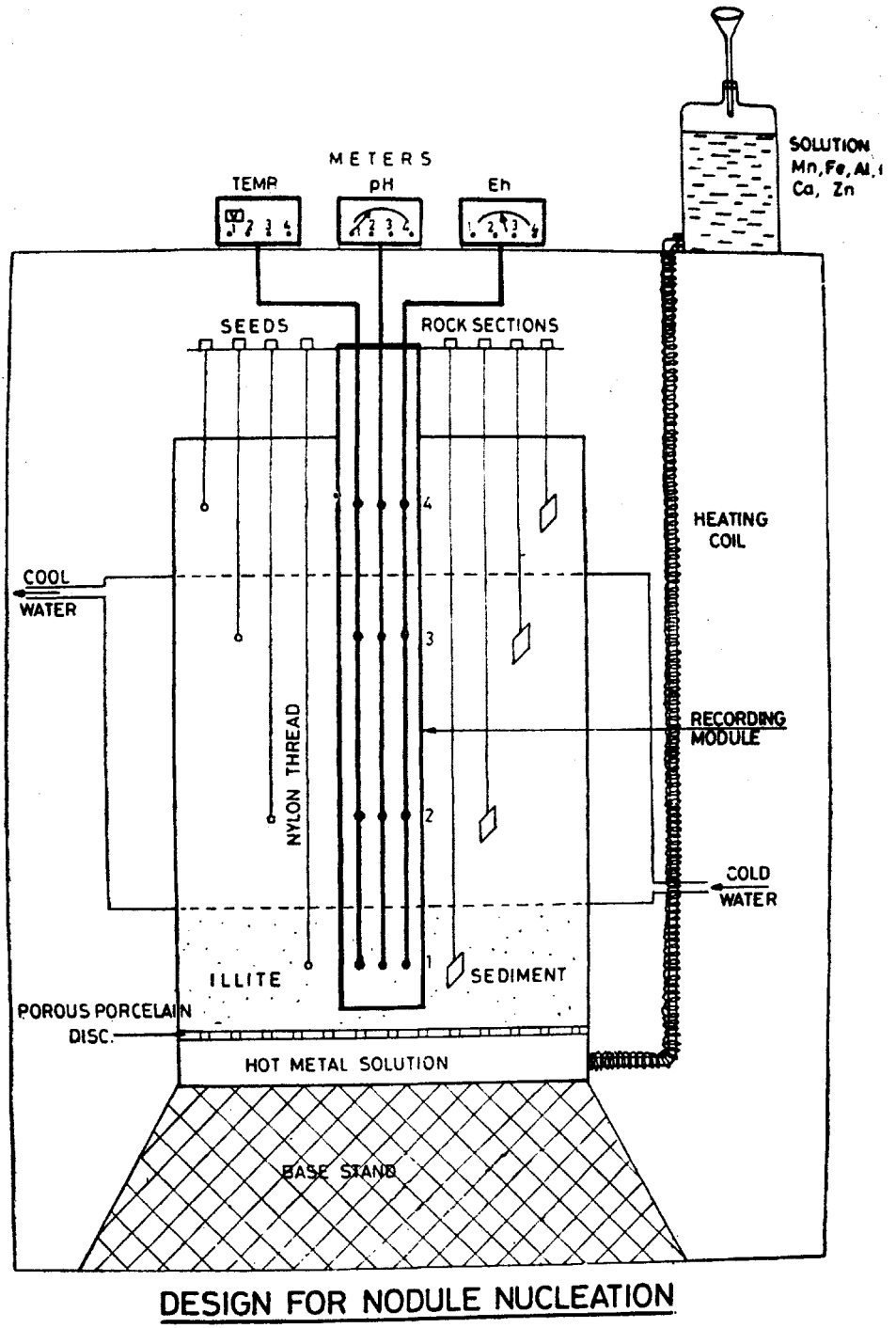

FIG 3 An alternative design of an experimental set-up for ferromanganese precipitation using a recording module.

may be introduced into the bottom of the nucleating chamber from a reserve stock. Seeds may be inserter at heights (depths), where module terminals are located. The most ideal seeds proposed are, bare thin section of various types of rock, consisting of different mineral assemblages, so that, even if the experiment fails to nucleate idealised nodules, the rate and pattern of precipitation of manganiferous constituents around various types of mineral grains in the thin sections can be noted and easily examined under a microscope. The conditions of the modified set-up is more similar to that of natural environment and the results obtained may be of greater practical significance.

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