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A brief overview on manganese nodules processing signifying the detail in the Indian context highlighting the international scenario

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ABSTRACT

Manganese nodules are the potential sources of base metals like copper, nickel, cobalt and manganese. Considerable research and development effort have been made all over the world to extract the metals from the manganese nodules during the past four decades. The paper summarizes the processes developed by various research and development organizations and metallurgical consortia for the extraction of metal values from the manganese nodules. Since copper, nickel and cobalt in the manganese nodules are in oxide forms and they are present in the lattices of iron and manganese minerals, these lattices are to be broken either by hydrometallurgical reduction or by reductive pyro-treatment for extraction of these metals. Based on this criterion, processing methods have been broadly divided into two categories: (i) pyrometallurgical treatment followed by hydrometallurgical processing and (ii) hydrometallurgical processing. Processes developed under these two categories have been discussed highlighting their merits and demerits. Pilot plant studies carried out by various metallurgical consortia like Kennecott Copper Corporation, Deep Sea Ventures, Metallurgical Hoboken Overpelt, and International Nickel Company are briefly described in this paper. The R&D efforts made in India in the processing of manganese nodules during last few decades are also discussed.

1. Introduction

Metals have invaluable contribution in the development of society since Bronze Age. Metals have been mostly exploited from ores and minerals available in earth crust and processed suitably for further use. As the depletion of suitable grade of land based ore bodies of important non-ferrous metals is posing an imminent threat to the society, the vast reserve of nodular concretions lying on the sea bed, which contain a number of important nonferrous metals, has created a lot of interest among the scientists and engineers (Haynes et al., 1985; Glover and Smith, 2003; Sen, 2010).

Polymetallic ocean nodules contain many valuable metals like Cu, Ni and Co besides trace amounts of Zn, Mo, Pb, V, Tl, Au, Pt, Ti, Zr, and rare earth elements like Ce, Nd, Dy etc. (Hein et al., 2013, Mohwinkel et al., 2014). These nodules were first discovered in 1868 in the Kara Sea, in the Arctic Ocean of Siberia (Monhemius, 1980). During the scientific expeditions of the HMS Challenger (1872–76), they were found to occur in most oceans of the world. Manganese being the major constituent, these nodules are generally called manganese nodules (MN). Besides manganese, nodules contain significant quantity of other base metals namely copper, nickel, cobalt, zinc etc. For this reason, nodules have been considered as potential alternative resource for Cu, Ni, Co and Mn metals to their terrestrial counterparts (Sen, 1999). Recently a comparison has been made by Hein et al. (2013) between the metal contents in manganese nodule to that in global terrestrial reserves base which are currently economical. It is found that tonnage of manganese, nickel and cobalt contained in Clarion–Clipperton Zone (CCZ) nodules exceed to that of land based reserves (Table 1). Nodules are found lying in millions of tons in all oceans of the world as loosely spread on sea floor (Sharma, 2011). These nodule abundant sites in the international waters are regulated by the International Seabed Authority (ISA) established under the UN Law of Sea. According to stipulations laid by ISA, eight 'Pioneer Investors' have been given exclusive rights for exploration. Among these, France, Russia, Japan, China, Intercontinental, Poland, Korea and Germany have rights in the Pacific Ocean and only India has rights in the Indian Ocean (Sharma, 2010).

The United Nations Ocean Economics and Technology Branch (UNOET) has laid down certain criteria for nodule mining which includes, (i) cut-off grade: 1.8% Ni + Cu, (ii) cut-off abundance: 5 kg/m^2, (iii) acceptable topography (<3^o slope), (iv) 20 years life time of a mine site, (v) annual recovery rate of 3 million t/yr (UNOET, 1987; Sharma, 2010). A number of processes, based on various metallurgical schemes, have been developed and flow-sheets are proposed for extraction of valuable metals from minable manganese nodules. Majority of these processes mainly focus on the recovery of Cu, Ni and Co leaving valuable manganese in the tailings/residues (Cardwell, 1973; Fuerstenau and Han, 1983, Hubred, 1980; Das and Anand, 1997; Kojima, 1997, Jana et al., 1999, Mukherjee et al., 2004a, 2004b). Among the several metallurgical

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Table 1
Estimated reserve of Cu, Ni, Co and Mn (Hein et al., 2013).

Metals	Reserves (million tons)	
	Global terrestrial reserve base	CCZ nodules
Mn	5200	5992
Ni	150	274
Cu	1000+	226
Co	13	44

consortia engaged in research and development of various aspects of metals recovery from deep-sea manganese nodules, significant work has been carried out by Kennecott Copper Corporation, Deep-Sea Ventures (DSV), Métallurgie Hoboken Overpelt and International Nickel Company (INCO) (Monhemius, 1980, Haynes et al., 1985; Sen, 1999, Jana, 2005). The R&D endeavor in India in the area of MN processing has been carried out mainly in CSIR-National Metallurgical Laboratory (CSIR-NML), Jamshedpur, CSIR-Institute of Minerals and Materials Technology (CSIR-IMMT), Bhubaneswar and Hindustan Zinc Limited (HZL), Udiapur (Premchand and Jana, 1999, Sen, 1999).

Since Cu, Ni and Co constitute about 2–3 wt.% of manganese nodules, generation of huge amounts of residue (about 70% of the MN treated) in above processes is inevitable. Significant efforts have been made to utilize manganese nodules process residue particularly that generated in the CSIR-IMMT and CSIR-NML processes (Randhawa, 2012). Residues have been successfully utilized for production of manganese ferro-alloys and different chemicals/metals.

This paper gives an overview of various processing routes available in the literature with regard to extractive metallurgy of manganese nodules. Initially, occurrence of manganese nodules and their general and mineralogical characteristics are discussed. Brief R&D work and details of processing routes developed and tested at pilot plant scale including that developed in India are described in this paper. Value addition by utilization of leached manganese nodules residue generated in IMMT and NML processes attempted at NML, Jamshedpur is also presented briefly. A comparative account on operational, economic and environmental aspects of different manganese nodules processing routes is also given in the concluding remarks.

2. Manganese nodules: occurrence and general characteristics

Manganese nodules are rock concretions of irregular shapes and sizes ranging from few mm to ~30 cm and form by concentric accumulation of Mn and Fe oxides around a nucleus (Hein et al., 2013). Image of some manganese nodules recovered from Indian Ocean is shown in Fig. 1. Major deposits are located mostly in areas of red clay or siliceous ooze, where the rate of detrital sedimentation is low. Horn et al. (1972) have developed a worldwide distribution list of manganese nodules. The North Pacific is the largest sedimentary basin in the world. The deep-sea red-clay region in the southwest corner of the North Atlantic has been identified as a potential area of abundant nodule deposits. In the Indian Ocean Basin, high concentrations of nodules have been found at bases of submarine ridges, sometimes in areas of major fault zones (Bezrukov and Andrushchenko, 1972). Cronan and Moorby (1976) suggested that the Central Indian Ocean Basin (CIOB) might be the most suitable site for manganese nodules accumulation of sufficient density. Manganese nodule deposits are also well distributed in the Barrents, Kara, White, and Baltic seas and the Gulf of Maine (Manheim, 1965). However, recent work suggests that nodules of economic interest have been found in three areas: the north central Pacific Ocean, the Peru Basin in the southeast Pacific, and the center of the north Indian Ocean (Glover and Smith, 2003). The average chemical composition of manganese nodule from Central Indian Ocean Basin is given in Table 2 (Mishra et al., 2011). The chemical composition of other oceans nodules with respect to Cu, Ni, Co, Mn and Fe, as reported by Sen (2010) is given in Table 3. It is apparent that all the nodules-rich sites are not minable

Fig. 1. (a) Manganese nodules obtained from Central Indian Ocean Basin and (b) magnified view of cross-section of manganese nodule.

according to UNEOT (Sharma, 2010). Apart from base metals, manganese nodules contain a host of other elements including rare earth metals (Haynes et al., 1985; Dubanin and Svalov, 2000). Extraction of some of these strategically important elements may boost the economics of nodule processing (Park et al., 2013; Parhi et al., 2013). Recent studies by Parhi et al. (2015) on separation of rare earth metals by solvent extraction put a step ahead in rare earth metal extraction from sea nodules.

Manganese nodules are very porous in nature and contain extremely fine pores of the order of 100 Å diameters. This often results in high moisture content of the nodules, usually about 30–40% by weight. Important physical characteristics of manganese nodules are summarized in Table 4 (Jana et al., 1997). Manganese nodules grow at a slowest rate of all geological phenomena—of the order of a millimeter to centimeter per million years and lie on the seabed sediment, often partly or completely buried (Monhemius, 1980; Glover and Smith, 2003, Hein and Koschinsky, 2014). The sizes vary from micro-nodules (<1 cm diameter) to nodules (1–15 cm diameter) and macro-nodules (>15 cm diameter) (Mukherjee et al., 2004a, 2004b). The unique physical

Table 2
Compositions of manganese nodules from Central Indian Ocean Basin (Mishra et al., 2011).

Constituents	Wt.%	Constituents	Wt.%
Cu	1.05	Zn	0.08
Ni	1.22	Mo	0.04
Co	0.073	SiO_2	16.00
Fe	6.72	Free moisture	13.67
Mn	23.25	Loss on ignition	28.10