Chapter 1

Introduction

Developing technology for the extraction of metals from lean ores is an area of extractive metallurgy that has gained considerable importance, because of the gradual depletion of terrestrial high-grade ore resources. Return on investment becomes a critical factor and the operation costs assume greater significance; of particular significance are the energy consumed and its associated costs, the grade of the ore being treated, options for byproduct recovery, and the relative price of the products. Many processes for treating lean ores have progressed to several million dollars worth of pilot plants, but not to an eventual commercialization due to a lack of appreciation of these critical factors. A process scheme needs to be optimized for simultaneously maximizing metal throughput and minimizing the direct operating costs incurred within constraints set for the operating variables. This leads to a multi-objective optimization problem. Since exploitation of low grade manganese resources would be of utmost importance to sustain several industrial processes, a typical low-grade manganese ore has been chosen in this study for the application of the optimization tool. The selected approaches studied in this work keeps in mind the future requirements of developing a viable process flowsheet for treating the low-grade manganese ores.

1.1 Importance of Manganese Bearing Resources

Manganese is ranked after iron, copper and aluminium in terms of global usage and considered to be one of the strategic metals. The application domain for manganese is bigger due to its usage in steel, batteries etc., where it provides a value addition to end products. The annual global manganese demand is being driven by the rapidly growing steel production, accounting for about 90% of the total manganese requirements [1, 2]. In the steel making sector it is consumed primarily as an alloying element. Global steel production has shown a tremendous growth in the last of the half a decade and is still growing. In 1950 the world steel production was about 200 Millon tons (Mt) and in 2006, the figure stood at 1,239.5 Mt [3]. In 2008, the global consumption of manganese based ferro alloys was approximately 10 kg/ton of steel produced, leading to a total consumption of 11.395 Mt. Energy industry is another major consumer of manganese where the rest 10% is used for various end products like manganese dioxides, dry batteries, manganese metal, chemical manganese dioxide (CMD) etc. Market share is growing strongly for various manganese products, driven mostly by steel industry.

Global manganese resources have been estimated as 5200 Mt (Million tonnes) but the resources are unequally spread. The majority of the resources are distributed in South Africa (approximately 80 %) and rest reserves being in Ukraine, Australia, Gabon, India and China [4,5]. Annual production rate is high (33.7 Mt in 2006, 11.8 Mt in manganese content). However, 40% of the total production has been from 40% from high grade resources (>44% Mn), 20% from medium grade resources (>30% < 44%) and rest from low grade resources (<30% Mn) [5,6].

Thus, the low and medium grade manganese resources must be exploited considering their potential and more precise effort is required, which is also applicable to the possible terrestrial resources. Polymetallic sea nodules are the most important reserve for manganese from ocean and can be categorized as a lean manganese bearing ore. Additionally, the presence of other metals like copper, nickel and cobalt make a strong case for the exploitation of the oceanic manganese deposits, which in consequence demands for more specific and appropriate technological growth. However, a large part of the reserve does not meet the required grade for efficient production of high grade ferromanganese alloys. Due to this there always remains a need for development of alternative technology leading to an extraction process for the lean resources.

A concentrated effort should be directed for development of proper and appropriate technology for extraction of manganese value from these low and medium grade resources. However, a large part of the reserve does not meet the required grade for efficient production of high grade ferromanganese alloys. Due to this there is always a need for development of alternative technology leading to an extraction process for the lean resources.

1.2 Low and Medium Grade Manganese Resources

Terrestrial ores

The manganese ores can be classified broadly on the basis of manganese content in the ore. Typically, the resources with more than 35% Mn are regarded as manganese bearing ores and the reserves containing about 10 - 35% Mn are categorized as low grade *ferruginous manganese ores*. The potential use of terrestrial reserves is for production of various end products of manganese like Electrolytic Manganese Dioxide (EMD), high purity manganese metal, ferroalloys etc. Most of the high grade ($> 40\%$) terrestrial reserves are used for production of ferroalloys and EMD. The different end products of manganese such as chemical manganese dioxide (CMD) and other chemicals requires different grade of manganese ores as starting raw material.

Ocean resources

An important ore under ferruginous manganese ores is polymetallic sea nodules. Deep-sea ferromanganese oxide deposits have received increasing attention in recent years [7]. The first existence of *ferromanganese sea nodules* was discovered several decades ago by H.M.S. *Challenger* during the period 1873-1876 [7]. Subsequently, with time a need driven interest and widespread curiosity towards exploration and extraction of metal values had made it to emerge as a potential mineral source.

Economic potential and associated metal values of nodules have been recognized within last 40 years, as described by Mero [7]. Halbach and Fellerer [5] in their study have projected some interesting comparison of metal reserves on land and the metal resources held up by the nodules. The ratio between the land and ocean based resources is approximately 1 for both nickel and manganese and 10 for copper; however for cobalt it is about 0.08. The reserves of cobalt is approximately 12 times more with respect to land reserves. Sea nodules can be considered as a high grade manganese resource in context of the relative price ratio of the associated metals with manganese. A greater profit margin could be achieved with relatively low grade manganese ores, if and only if it is associated with high value added metals. Due to this reason, Ferromanganese nodules are becoming a potential source of not only manganese but also for its associated metal values.

Composition of Sea Nodules. Composition of the nodules varies significantly from various areas of extraction and depends upon associated mineralogy as reported by Glasby [7] and provided in Table 1.1. It is appropriate to analyze the mineralogy and variability of the nodules phases with respect to its processing operations. The polymetallic nodules with a low Mn/Fe ratio (0.73–0.88) need to be mixed with a richer manganese ore for processing further. Sea nodules with ratios of Mn/Fe 2.5 with manganese content between 20-25% are amenable for further processing.

Table 1.1: Composition of polymetallic nodules from various extraction basins

Component	S.W. Pacific Basin	Samoan Basin	C-C F.Z.	Peru Basin
$Mn\%$	16.6	17.3	29.1	33.1
$Fe\%$	22.8	19.6	5.4	7.1
$Co\%$	0.44	0.23	0.23	0.09
$Ni\%$	0.35	0.23	1.29	1.4
$Cu\%$	0.21	0.17	1.19	0.69
Mn/Fe	0.73	0.88	5.4	4.7

1.3 Manganese:Usage Pattern & Relevance to Optimization Approaches

A low grade resource for manganese needs to be carefully processed to final products, so that the overall product value can be maximized. For example, due to the presence of copper, nickel and cobalt in addition to manganese in sea nodules, the total metallic value needs to be extracted to maximize the profit margin. The ferroalloy contains nickel, copper, cobalt and manganese which are priced at \$12/kg, \$ 4/kg, \$20/kg and \$ 0.8/kg respectively [5]. Hence, the manganese bears almost 48% of the total metal valuation of the nodules for the pacific grade nodules. The valuation of the manganese bearing products depend on the demand of it and on the relative price of the copper, nickel and cobalt products.

Presently the usage pattern of manganese is directed towards the steel making sector where it gets consumed as ferroalloys. The consumption profile for ferroalloys rose from 10.5 Million ton in 2005 to 11.7 Million ton in 2007, with a growth rate of almost 10% [5, 6]. Present usage of manganese in steel sector provides an important fact that manganese intensive steel grades are expected to grow at much higher rate in comparison to low manganese steels.

Electrolytic Manganese Dioxide (EMD) is another major consumer of manganese, which is expected to grow rapidly because of the global boom in energy sector. The existing global production rate of EMD is approximately close to 400,000 MT per annum [5, 8] and in future the expected growth rate can even exceed the value of 4%. This rapid growth rate is because of growing battery markets, such as Li/MnO_2 primary cells and Li-ion secondary cells using $LiMn_2O_4$ which consumes EMD as raw material. It even finds the application in non-battery production sector like, manufacturing of ferrites [5]. But the market for ferrites is presently small and are expected to grow similar to other high value sectors. The raw material for soft ferrite has shown a global production of 50,000 MT in 2005.

Thus, there lies a numerous usage of manganese alloys and compounds; such as the production of these alloys, compounds and metals which are linked not only to the availability but also to the grade of the resources. In this context the diverse compositions of low grade ores reserves becomes important. This present scenario has consequently generated the necessity of dealing with these lean manganese ores as the primary resources, not only to meet the demands but also to optimize flowsheets. Even with growing steel sector, the production of ferroalloys should be the major development thrust, but the emphasis should even be on production of EMD and other products for better value addition of the product mix. The production of these alloys, compounds and metals is linked to the manganese content in the ore and even the process route for recovery of the elements.

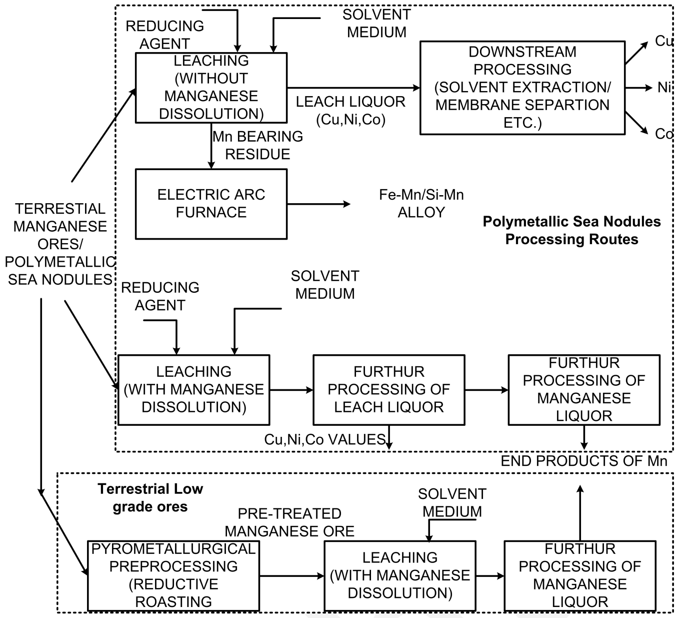

Figure 1.1: Processing route for reductive leaching of polymetallic sea nodules

1.4 Processing of Lean Manganese Bearing Ores

Developing technology for the extraction of metals from lean ores is an area of extractive metallurgy that has gained considerable importance,because of the gradual depletion of high-grade terrestrial resources. Extraction of metallic values from these resources is conducted either by pyro-hydro processing route or by directly using reductive leaching through hydrometallurgical route. Processing of ores in various process routes are presented below.

In case of deep sea nodules, the decision needs to be taken in respect of other metals that are to be recovered apart from manganese. Evidently it is clear from the composition of nodules that other than manganese, Cu, Ni and Co contribute to more than 50% of total metallic value. Due to this reason, there needs to be an efficient processing route for extraction of metals so that the overall process is viable and at the same time making the extraction of metallic values like Cu, Ni and Co successful, which are present in correlation with the manganese and iron phases. Since Co value is distributed between manganese and iron bearing phases, the chemistry of extraction needs to be designed in such a manner that it should be able to extract manganese as well as other metal values. Various processing routes for extraction of metallic values from lean manganese bearing resources are discussed in brief and a schematic diagram is presented in Fig. 1.1.

1.4.1 Terrestrial manganese ores

Till date, hydrometallurgy has been able to provide comparatively more viable process routes for the extraction of these category of manganese ores. The typical leaching process involves reductive leaching of the metallic values in leach liquor with the use of various kinds of reducing agents as described below in addition to a broad view of pyro-hydro treatment routes. Various processing schemes for lean terrestrial manganese ores are shown in Fig. 1.1.

Hydrometallurgical processing schemes

Reductive leaching

Manganese bering ores have been treated with acidified ferrous sulfate or pickle liquors [9,10]. US Bureau of Mines [11] has developed a novel process route for extraction of manganese values from lean resources using pickle liquor (weak $FeSO_4$-H_2SO_4-$(NH_4)_2SO_4$ solutions). Das et.al [9], has shown how the MnO_2 in the ore reacts with ferrous sulphate and achieved manganese recovery of 90% with a stoichiometric amount of ferrous sulfate at 90^{o}C for an hour with solid-liquid ratio of 1:10. The gelatinous condition of the leach slurry causes the main problem with the filtration operation. To avoid this, sulfuric acid is added to make the filtration process much easier with greater Mn extraction, but with three-four fold much iron reporting in the solution [9].

Extraction of metallic values from low grade manganese resources using sulfur dioxide is one most widely studied process. Petrie [12] in his study has shown the reaction mechanism and various reaction steps which occur during dissolution of manganese in the solution. Sulfur dioxide in the solution is oxidized to SO_4^{2-} and dithionate; depending on the pH, temperature and redox potential of leaching solution. Dithionate based process was developed to recover manganese from low grade ores [13]. Advantage regarding this process is to utilize the dithionate intermediate product of the reductive reaction to stabilize both the reduced Mn(II) and calcium in the solution. A study was conducted by Naik et al. [14,15] for low grade manganese ores by controlled diffusion of SO_2 to the reaction surface. During the process, twice the stoichiometric quantity of SO_2 was required for dissolution of manganese from its host matrix.

Organic reductants like sawdust [16], glucose [17], sucrose [18], lactose [19], glycerine [20] and even organic acids like oxalic acid, citric acid, tartaric acid, formic acid [21, 22] were also used. Out of these reductants listed, carbohydrate reductants are considered to be cost effective and non–hazardous and even can be used either in pure form or in form of waste stream. The reaction stoichiometry was proposed as follows.

$$12MnO_2 + C_6H_{12}O_6 + 12H_2SO_4 \rightarrow 6CO_2 + 12MnSO_4 + 18H_2O$$

The only problem with this processing route is high emission of carbon dioxide during the leaching step, which might make the process unfavorable due to the strict environmental constraints. Doyle and Bodine [23] have used coal for reduction of manganese from the solution. The manganese in the dissolved liquor is first adsorbed on the coal surface and subsequently gets reduced from its higher oxidation state to lower one. In the study, the authors has reduced Mn(IV) and Mn(II), which gets adsorbed on coal surface and probably forms a manganese oxide surface layer. Various parameters like oxidation treatment, metal ion concentration, and solution pH on metal kinetics and coal loading were investigated in the study. Potential application of coal can be seen for extraction of metallic values from lean manganese bearing resources.

Manganese pyro-hydrometallurgy processing routes

The hydrometallurgical processing routes with pyrometallurgical pre-treatment steps hold an important role in extraction of metallic values from lean manganese ores. During the pyrometallurgical pre-treatment step, the host matrix gets reduced followed by hydrometallurgical reductive dissolution which is an essential step for extraction of metals from the reduced matrix. Smelting or reduction roasting followed by leaching is by far the most commonly employed method in manganese industry as shown in [24]. In this study, the authors have adopted reduction roasting of the manganese ore containing about 50-52% manganese in reducing atmosphere of CO-H_2. The partially reduced ore obtained from pyrometallurgical operation is subjected to leaching in sulfuric acid medium. This study was performed for very high manganese content in the ore, so it cannot be categorized under low grade processing route. However, similar route can even be adopted for lean manganese bearing ores which contains about 20-25% Mn. The main disadvantage of this process is its high temperature operation and emission of harmful gases into the environment. In case of reductive roasting for lean manganese resources, it requires a reaction temperature of about 800^{o}C, which is very high and most reactors cannot sustain it and during the process more fuel is consumed [25]. To make the process of reduction roasting environmental friendly, Zhuo Cheng et. al [25] have used cornstalk as reductant for reduction roasting for lean manganese ores and followed it by sulfuric acid leaching of the roasted ore. Various process parameters like weight ratio of ore to cornstalk, roasting temperature, roasting time, ore particle size, leaching temperature, stirring speed and sulfuric acid concentration on the leaching recovery were analyzed. Manganese recovery reached 90.2% under optimal condition with manganese dioxide ore to cornstalk weight ratio of 10:3, roasting temperature of 500^{o}C for 80 minutes, leaching stirring speed of 400 revolutions per minute, sulfuric acid concentration of 3 mol/l, leaching temperature of 50^{o}C for 40 minutes. Other than reductive roasting as primary pyrometallurgical route, other pre-treatment steps like smelting [26], sulphatising [27] etc. can even be practiced. In combination with hydrometallurgical processing route efficient extraction of metallic values can be achieved, but the process would consume more energy. Various process routes are followed for reduction like in presence of sulfuric acid or ammonium sulfate to convert the manganese minerals to soluble sulfates, sulphation of manganese ore in gaseous SO_2 environment [4].

Direct smelting route for extraction of manganese value from high grade manganese ores (>40%) is a popular practice for production of ferromanganese alloys, but for the case of lean manganese ore, it is not considered as a viable option due to the high energy consumption per ton of metallic product.

1.4.2 Polymetallic sea nodules

The composition of sea nodules show that manganese shares more than 50% metallic values in the ore. It was realized much earlier that manganese value constitutes 55% of the total metallic values in sea nodules (reported total value of manganese nodule as $189/short ton, 1979, with contained manganese value as $105) [5]. The earlier preferred approach was to extract the non-manganese metallic values like

Cu, Ni and Co and dump the rest as residue. This lead to the *three metal* recovery process *without the option of manganese recovery*. The techno-economics studies for the processing route for three metal case has established that such a plant will require a high capital cost and additional cost for dumping the leach residue. This type of processing approach was not conducive to an early commercialization of a sea nodules venture. To bring down the capital investment and to increase the revenue generation from metal values, the *four metal* option has been developed. The importance of developing routes based on extraction of four metals has also been stressed by Habashi [28]. He has pointed out that the supply-demand considerations coupled with strategic considerations related to recovery of Cu, Ni, Co and Mn may be eventually be decisive in future exploration of the sea nodules resources. Earlier work performed by different mining consortium have considered primarily the extraction processes for copper, nickel and cobalt [28]. The importance of recovering manganese from low grade manganese resources have led to re-evaluation of manganese recovery processes for sea nodules. Thus, four metal based processes from sea nodules are now being actively considered. Along with recovery of other metallic values, the manganese can be recovered either from the leach residue or by dissolution of manganese from sea nodules along with other metallic values in the leach liquor. Manganese dissolved in the leach liquor is further processed to form end products of manganese. Thus, the main process routes which are followed for the recovery of manganese and other metal values are listed below:

- Reductive leaching of manganese nodules.
- Leach residue smelting practice.

Additionally, it is possible to recover manganese from sea nodules by direct smelting of sea nodules and producing a manganese rich slag. The slag can be further treated for ferroalloy recovery [5]. The main focus of the review orients towards the recovery of manganese and other metallic values by reductive leaching routes in various mediums.

Reductive leaching of polymetallic sea nodules

Manganese bearing nodules are subjected to reductive leaching route for extraction of metallic values like copper, nickel and cobalt along with manganese which holds the major share in the nodules. Manganese in the nodules is extracted either as residue which is devoid of other metallic values or in the leach liquor along with the other metallic values. Such process routes for extraction of manganese and its allied metallic values are presented in Fig. 1.1.

Reductive leaching in solution with generation of manganese bearing residue

Various processes, developed for extraction of metallic values from nodules like Cu, Ni and Co in the solution along with the generation of manganese rich residue needs to be reviewed.

"Cuprion Process" proposed by Kennecott Copper Corporation is one of the popular and best studied process in this group. The reduction is carried out in aqueous phase by generating Syngas [29]. A recycle stream of metal carbonate was preferred for monitoring the desired level of cuprous ions in the leaching reactor.Another version for elevated pressure has been reported in the literature [30], but the data was not available regarding its scale up. Process modeling of the leaching step was undertaken [5], considering the leaching reactions as:

$$MnO_2 + 2Cu(NH_3)^{2+} + 6NH_3 + CO_2 + H_2O \rightarrow MnCO_3 + 2Cu(NH_3)_4^{2+} + 2OH^-$$

$$2Cu(NH_3)_4^{2+} + CO + 2OH^- \rightarrow 2Cu(NH_3)^{2+} + 6NH_3 + CO_2 + H_2O$$

The net overall reaction is thus :

$$MnO_2 + CO \rightarrow MnCO_3$$

The copper ions in the solution are considered as catalyst for the above reactions and in the absence of these ions the reactions cannot proceed.

In another process, leaching of nodules in ammoniacal medium using sulphur-dioxide as reductant was developed by Regional Research Laboratory, (presently Institute of Minerals and Materials Technology (IMMT)) Bhubaneswar, India. The process developed was even piloted, commissioned and operated [31, 32] for 500 kg/day capacity for testing the process regarding high scale recovery issues. The leaching reactions along with other reactions are shown below, it should be noticed that the manganese in the nodules report to the residue. Some part of the manganese which gets dissolved was recovered in demanganization step as manganese cake containing about 55% of manganese. Other metallic values get dissolved in the solution and recovered downstream. The reactions are:

1. Ammonia and sulfur dioxide gas mixing and reaction
   (a) $SO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2 SO_3$
2. Leaching
   (a) $MnO_2 + (NH_4)_2 SO_3 \rightarrow MnO + (NH_4)_2 SO_4$
   (b) $MnO + 2NH_3 + (NH_4)_2 SO_4 \rightarrow Mn (NH_3)_4 SO_4 + H_2O$
   (c) $CuO + 2NH_3 + (NH_4)_2 SO_4 \rightarrow Cu (NH_3)_4 SO_4 + H_2O$
   (d) $NiO + 2NH_3 + (NH_4)_2 SO_4 \rightarrow Ni (NH_3)_4 SO_4 + H_2O$
   (e) $Co_3O_4 + (NH_4)_2 SO_3 \rightarrow 3CoO + (NH_4)_2 SO_4$
   (f) $CoO + 2NH_3 + (NH_4)_2 SO_4 \rightarrow Co (NH_3)_4 SO_4 + H_2O$
3. Demanganization
   (a) $Mn (NH_3)_4 SO_4 + 0.5O_2 + H_2O \rightarrow MnO_2 + (NH_4)_2 SO_4 + 2NH_3$

The manganese, reported in the form of MnO_2 in nodules has to be first reduced to MnO, which in a way librates the other metal oxide phases that are very finely dispersed in the MnO_2 matrix. These reactions are basically carried out in the leaching circuit of the flowsheet forming various metal ammine complexes. Particular reactor conditions are maintained, keeping the reactor exit concentrations of ammonia and ammonium sulfate constant. The dissolved manganese is again oxidized and precipitated in a downstream process called demanganization by sparging oxygen into a reactor to recover the manganese as MnO_2. Transformation of MnO_2 to MnO occurs in the solid matrix, the reaction is comparatively faster than dissolution of MnO to leach liquor.

Sulphuric acid leaching. The pressure leaching process route using sulfuric acid proves to be an attractive option to selectively leach out Cu, Ni and Co from the ore matrix and leaving manganese in the residue. The acid leaching process was critically analyzed by many researchers [33]. In context of the acid leaching routes, the main jubilance was encouraged by the similarity of nodules to land based nickel laterite ores, that are treated by acid pressure leaching. In comparison to study performed by Han [5], who achieved a substantial nickel and copper recoveries with oxygen partial pressure of 100 psi (total pressure 300 psig), initial pH of 1.63 and a leaching reaction time of 60 minutes, Ulrich [5] reached even higher recoveries by varying the leaching conditions. Both of the works have reported a moderate recovery value for cobalt. In another study, performed by US Bureau of Mines [34], the recoveries for Ni, Cu and Co was claimed to be approximately 90% at high pressure of leaching (about 35 atm) and 245^{o}C. To minimize the scale formation during high temperature leaching operation, Subramanium et al. [35] in a study, carried out a two stage leaching process at INCO which got patented. In the first stage, the leaching temperature was kept at 100^{o}C to consume most of the acidity and later in the second stage, the leaching temperature was raised to dissolve valuable metallic contents.

French researchers have shown an interesting preprocessing to acid leaching by including a preheating stage followed by a medium temperature leaching (180^{o}C) operation [5]. The advantage of two stage process has avoided the similar high temperature pressure leaching process routes followed for lateritic ores [5]. The process route, Messer CEA, France, has operated a pilot plant during the 1980's at the capacity of 5 kg/h of nodules and high metal recoveries were consistently reported.

Manganese recovery without generating manganese residue : The case of complete manganese dissolution

Manganese present in the nodules can be recovered by designing the process chemistry in such a way that manganese dissolution occurs along with other metallic values or whole of manganese reports to the residue, while other metallic values go into leaching medium. This section concentrate on the dissolution chemistry for options of manganese recovery from nodules without generation of any manganese residue. Manganese dissolution from nodules can be performed either with or without reducing agent. It has been observed that without reducing agent, dissolution rate is very slow and requires very high retention time of nodules in the autoclave. The main concept which is adopted during the reductive leaching of nodules is that whole of the manganese from the nodules get in the solution during the leaching process. As no manganese rich residue is generated, the smelting operation can be bypassed. Different process routes have been reported in literature regarding the reductive leaching in solution for complete solubilization of manganese along with other metallic values.

Reductive leaching with sulfur dioxide. The recent studies have reported reductive leaching of nodules in solution, causing dissolution of manganese along with other metallic values. Khalafalla [36, 37], has used the aqueous SO_2 in acidic medium for leaching of sea nodules. In his study, the SO_2 has been used as reductant which holds an added advantage over other reductant in terms of its rapid rate of reaction, low temperature operation, easy purification of leach liquor and elimination of residue as well as barren solution disposal problem. Sulfur dioxide is cheaper to produce and can even be extracted from spent gas of smelters. This work by Khalafalla has motivated many other researchers to explore various reducing agents for nodules/wad leaching [38, 39].

In another study, Acharya et al. [40] carried out leaching exercise in an aqueous SO_2 -H_2SO_4- $(NH_4)_2SO_4$ system for dissolution of metallic values (Mn, Cu, Ni, Co and Zn) from sea nodules. In this study the authors have tried to avoid the iron dissolution in leach liquor. The leaching parameters such has sulphuric acid concentration, ammonium sulphate concentration, time and pulp density were varied systematically to obtain a better dissolution behavior of metallic values. The results even report that presence of both sulphuric acid and SO_2 has enhanced the recovery of Cu, Ni, Co and Mn. The optimum recoveries reported for the leach process for various metals are 88.5% Cu, 99.8% Ni, 91.8% Co and 99.6% Mn. The various reactions in presence of aqueous SO_2 are provided below.

1. $MnO_2 + H_2SO_3 \rightarrow MnSO_4 + H_2O$
2. $Co_2O_3 + H_2SO_3 + H_2SO_4 \rightarrow 2CoSO_4 + 2H_2O$

3. $Ni_2O_3 + H_2SO_3 + H_2SO_4 \rightarrow 2NiSO_4 + 2H_2O$

There lies a strong dependency between leaching and ratio of actual moles of SO_2 in the solution to the weight of ground nodules, which triggers the selective dissolution of Ni, Co and Mn over Cu, Fe and Al [41]. The specific ratio of sulfur dioxide to nodules will vary according to the grade as well amount of nodules. A similar kind of study has been performed by Kanungo and Das [42] in presence of aqueous sulfur dioxide as reducing agent. The tetravalent manganese oxide is reduced rapidly in course of the reductive dissolution, and it is extracted along with others. As projected by the study of Pahlman and Khalafalla [41], the extraction of copper and iron is dependent on the ratio of sulfur dioxide to nodules. With a correct combination of this ratio and leaching time, more than 85% of Mn, Ni, Co and more than 75% of Cu could be extracted with small recovery of iron in the solution. In the initial stages, leaching was extremely fast but with prolonged leaching time, the in-situ separation of iron from the leach liquor is possible. Particle size fractions and leaching conditions are the two critical factors for optimum recovery of metal values. The authors have shown that for Indian ocean nodules which are low in copper, such selective leaching may not be economical.

Anand et. al [39] attempted to control manganese dissolution at elevated temperature and pressure in presence of oxygen in dilute sulfuric acid medium along with other metallic values. To achieve extraction of Cu, Ni, Co and Mn, charcoal was used as the reductant for reduction of manganese from higher manganese oxidation state to manganese sulphate. The recoveries for Cu, Ni, Co and Mn were 77%, 99.8%, 88% and 99.8% respectively under optimum leaching conditions.

Another study was performed by Canterford [38], on manganese wad in sulfuric acid medium for extraction of metallic values. Manganese wad is low grade resource of mostly cobalt and manganese. In his study, manganese wad from the Mt. Tabor region of Queensland, Australia, was used which contains 1% cobalt with lesser copper and nickel. Due to existing similarities between the manganese nodules and manganese wad, the process routes developed for manganese wad is applicable for nodules. Sulfuric acid route at atmospheric pressure and ambient temperature is considered as a potential route. The studies have been performed using the pug, agitated tank and column techniques. The main conclusion which was drawn from the study is, that the dissolution rate of metal values (Cu, Ni and Co) from wad is extremely slow, even in presence of excess acid. From the above results of the experiments, it was concluded that with such a low leaching rate, this kind of technological route can not be commercially viable.

Reductive leaching with organic and other reductants. Aromatic reagents like phenol have been used as a reducing agent in dilute sulfuric acid medium [43]. Six phenols, including hydroxybenzene, o-dihydroxybenzene,m-dihydroxybenzene, p-dihydroxybenzene, o-trihydroxybenzene and m-trihydroxybenzene, were tested as reducing agents. The results of leaching test have shown that all the phenols work effectively as reducing agents that influence the leach chemistry and consequently increase the rate of extraction of Mn, Cu, Ni and Co from the sea nodules. The rate of leaching is effectively fast and about 95% of metallic values can be extracted in 10 - 20 minutes of leaching time in ambient temperature and pressure conditions.

Allen et. al [44] in their study used hydrogen peroxide ($\mathrm{H_2O_2}$) as a reducing agent in dilute sulfuric acid medium for leaching sea nodules. The observed leaching rate is very fast and metal extraction is reported to be complete in about 5 minutes time. The main advantage with this reduction route is it's environment friendly nature, as it produces water and oxygen as byproducts of leaching. Reductive dissolution follows the same stichometric reaction:

$$MnO_2 + H_2O_2 + 2H^+ \rightleftharpoons Mn^{2+} + 2H_2O + O_2$$

Leaching with spent electrolyte containing reductants. Spent electrolytes can even be used to leach sea nodules as shown in a two stage reductive process route developed by Kane and Cardwell [45]. In the first stage of leaching, spent electrolytes contain approximately 4% free acid, which was used to leach nodules for 14 hours at leaching temperature of 40–80^{o}C for preferential extraction of nickel and copper values. During the second stage, the filtered solids were leached with solution containing about 100 g/l of $FeSO_4$ at 50-60^{o}C and at pH 3 - 4 to extract rest of metallic values (Mn and Co). The important issue which needs to be addressed is that 100% separation of Cu and Ni cannot be achieved in first stage, about 80% each of copper and nickel could be leached. Along with dissolution of cobalt and manganese, the traces of nickel is also present in the leaching solution obtained from second stage.

In more recent times, a study reported by Vu et. al [10] is regarding the leaching of sea nodules with acidic $FeSO_4$ solution. Very high recoveries of all metals are reported, as more than 85% Co and 90% of Ni, Cu and Mn could be extracted in 30 minutes of leaching time. The leaching parameters like sulphuric acid concentration, liquid-to-solid ratio, temperature, time and particle size of nodules were varied to study their effect on metal recoveries. Very high recoveries of all the metals were obtained, but the solution contained high levels of iron since greater than stoichiometric quantity of acid was used.

Primary advantage with two stage leaching process over non-selective leaching process is, nickel is separated from cobalt at early leaching stages and the subsequent process is much simpler to operate on. But the main drawback is due to high energy consumption in leaching stage over selective leaching. The applicability of the process is largely dependent on the valuable composition of the metals in the nodules as well as availability of cheap spent industrial pickle liquors.

Smelting practice for manganese leach residue

Manganese rich residue obtained from leaching stage, which is although poorer in manganese as compared to terrestrial ores, can be smelted through similar route. However, it is necessary to follow the two-slag practice. The pyrometallurgical route for smelting approaches for sea nodules or generated residue is another viable option for recovery of manganese bearing products [5]. The manganese bearing residue that is generated contains mostly manganese with traces of other metals like copper, nickel and cobalt. It could be appropriate to compare the smelting practice of sea nodules or residue with that of the terrestrial manganese ores. The smelting of a typical metallurgical grade manganese ore containing 48.6% Mn, 3.8% Fe, 4% Al_2O_3 and about 6.8% silica, is considered favorable if Mn:Fe ratio is 6:1 [46]. High carbon or medium carbon ferromnaganese alloy is produced by direct smelting practice of terrestrial manganese bearing ores in electric arc furnace. The resulting slag can even be smelted to produce ferromanganese [46].

In case for sea nodules or manganese residue, the ratio between $Mn : Fe$ is adverse. So to produce the manganese bearing end products, a two stage smelting practice is must. During two stage smelting practice, it involves re-smelting of the first slag. During the first stage of smelting, the primary aim is to produce a slag with enriched Mn:Fe ratio and in process, the product of this practice is iron rich alloy phase in place of ferromanganese alloy. Manganese in the nodules or residue is less reduced and reports in the slag which is smelted in second stage to produce desired product of manganese. The slag obtained from first smelting is enriched to $Mn : Fe$ ratio of 6:1 which is ideal for production of high grade ferromanganese or silicomanganese alloys. During smelting of sea nodules, in the first stage along with iron in metallic phase, Cu, Ni and Co also reports to form a alloy, rich in all these metals. But while smelting the leach residue, the metallic phase produced mostly contains iron with very little traces of other metals [5].

Very less information is available about the direct or two stage smelting of manganese rich residue generated from leaching. The product of first stage smelting is pig iron as reported by the study performed by Lenoble [47]. During the second stage smelting operation, conducted in carbon bed furnace to possibly reduce the loss of manganese in the slag and thus resulting in higher recovery of manganese in alloy.

The main concern with production of ferroalloys from lean manganese grade resources is relatively higher power consumption per ton of alloy produced than its counterpart. The high requirement of power is due to two stage smelting practice as well as higher slag/alloy ratio of the final product. To reduce high energy consumption pertaining to two stages (8000 KWh/ton of final alloy), a high temperature pre-reduction or leaching step may be incorporated, which will reduce the host matrix partially.

Preparation of Electrolytic Manganese Dioxide from leach liquor

Electrolytic Manganese Dioxide (EMD) can be produced from purified leach liquor containing manganese sulphate, which is free from impurities of iron and other compounds. EMD can be prepared either from high grade manganese ores ($>$ 45% Mn) or from manganese carbonate ores. Due to involvement of reduction roasting step, there is emission of harmful gases and other metal ions into the environment. To avoid these process steps, the EMD can be produced from lean and medium garde manganese ores via hydrometallurgical process routes, which potentially avoid these kind of environmental issues. In the process of production of EMD from lean manganese bearing ores and tailings, the best suitable process is reductive leaching followed by liquor purification, neutralization and subsequently electrowining. For lean manganese ores, hydrometallurgical process is favorable over pyro-hydro process due to involvement of high reduction temperature and emission of harmful gases. EMD is prepared from the electrolytic process of acidified manganese solution and can be summarized from the following reactions:

- Anode : $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$
- Cathode : $2H^+ + 2e^- \rightarrow H_2$
- Overall : $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2$

In this process, the sulfuric acid is generated at anode and subsequently the acid is recycled back into leaching section. The electrolytic cell needs to be maintained at certain conditions of $MnSO_4$ and H_2SO_4 for efficiently producing EMD. The electrolyte is pumped through the cells at such a rate that the outlet concentration is 50 g/L $MnSO_4$ and 67 g/L H_2SO_4. The anolyte from the cell is returned to the leaching section along with some fresh acid which is added externally.

1.5 Implications of Previous Work: Scope of the Present Work

1.5.1 Flowsheet optimization for nodules processing

A detailed review of all the process routes testify that till date the main focus is towards the development of different reducing agents and leaching practice. Various studies performed till date considered the use of use of variety of leaching agents for enhancing the recovery of various metallic values from the ores [48]. Current research efforts have globally realized the importance of efficient recovery (with low operating cost), although, these have scarcely been directed towards flow sheet development and subsequent testing for commercial viability. A major challenge in process design is to assess the viability of processing such a widely varying grade of an oceanic low grade manganese resource for recovery of manganese and other valuable metals. Any process scheme developed for multi metal recovery would need to be assessed from the angle of sensitivity of the proposed scheme to metal throughput and direct chemical costs incurred with input ore grade variation. As any developed process scheme would have certain constraints with regard to the operating variables, the proposed scheme could be optimal only for a certain range of input grades of the raw materials. Chemical composition of these nodules changes from location to location across the vast sea bed. Manganese, which is present as manganese dioxide, is the major metallic component, varying over a wide range of 17 % to 30 %. Other associated metals present in the nodule matrix are of lower proportions in comparison to manganese. The composition of medium grade sea nodules on average vary between Mn: 17 - 28%, Cu: 0.5 - 1.3 %, Ni: 0.5 - 1.3% and Co: 0.1- 0.26%. Higher grade sea nodules, as is typically displayed for Pacific sea nodule, have the range of Mn: 24 - 30%, Cu: 0.8 - 1.4%, Ni: 0.8 - 1.4% and Co: 0.16 - 0.26%. The objective of the work is two folds: (a) To bring into focus the methodology for choosing an appropriate ore grade range for a given process flow sheet, and (b) Development and optimization of process routes for extraction of manganese values from lean manganese ores like sea nodules. As any developed process scheme would have certain constraints with regard to the operating variables, the proposed scheme could be optimal only for a certain range of input grades of the raw materials. Use of a process optimization strategy would be a vital requirement for that. Pareto optimal solutions [49] can be developed and appropriate decisions regarding the varying grades of raw material to be used for a given flow sheet can then be arrived at. Only use of different optimal solutions, however, may not permit choice of the input grade of nodules; indicative profitability for the different input grades for a given flow sheet under known recovery conditions would be useful to arrive at decisions with respect to ore grades. To find the right decision with such complex selection process the indicative cost model could to appropriate to narrow down the search with selection of right kind of grades.

1.5.2 Dissolution kinetics: Data driven modeling approach

Very few studies have been performed for understand the dissolution behavior of metallurgical ores with neural network models and even the data regarding the dissolution behavior for low grade ores is not provided. To analyze this, some neural network models which are applied for dissolution kinetics in metallurgical industry are provided.

In a methodology proposed by Rademan et.al [50] for analysis of an ill-defined and poorly understood leaching process from historical data, artificial neural model and statistical techniques have been used. In the process of development of neural network model, it was found that most effective process models were produced by the technique of Learning Vector Quantization (LVQ) neural network and a back propagation neural network. For the studies performed, the LVQ network model were able to classify correctly the outputs of the process with an accuracy of between 75% and 82%. The neural network developed, was even used to perform sensitivity analysis on the different process variables used during the leaching operation.

A neural network based analysis has been performed for leaching behavior of gold ore [51]. The intricate relationship between the mineral liberation and leaching of gold ore is poorly understood because of involvement of many complicated process. In this study, the authors have developed an artificial neural network to analyze and diagnose leaching data of gold ores obtained from gold mines in South Africa. A self-organizing neural net with a Kohonen layer was used for the following purpose.

In another study [52], the authors have tried to predict the leaching recovery of alumina in Bayer process from the chemical modules of bauxite fed to the process, using regression and Artificial Neural Network (ANN) methods. In modeling the leaching behavior by neural model, a data base of 332 sample analysis for bauxite and its subsequent red mud was created.

Another popular technique in data driven modeling is Genetic Programming (GP), which is an evolutionary based technique [49, 53–56]. But very few applications of GP can be found in chemical and metallurgical sectors [57–62]. Till date only one study has been found in extractive metallurgical sector where GP was successfully used. In the following study performed by Greeff and Aldrich [61], they used evolutionary programming for two leaching experiments performed. The first application is regarding acid pressure leaching of nickeliferous chromites ore, and the rest is on leaching of uranium and radium. The models developed were based on the input-output data relationship. These empirical models appropriately can predict the system behavior with variation of process parameters in input.

All the data driven models which were developed in the past for analysis of complex leaching process data were developed till the stage of data prediction, but there is no work done regarding optimization of these models. Even data from most of the industrial complex process are noisy, so the data driven models should have some kind of provision to avoid noise in the data. All the models on neural network which have been reviewed till date do not have such provision to avoid the noise in the data. All of the neural network models tried till date work on the basis on fixed architecture of the network, which backfires in case of noisy and sparse data and models fails to replicate the system behavior correctly. To bridge this gap in the work, here the efforts have been directed towards using an evolutionary neural network model and GP based model to analyze the dissolution kinetics data of lean manganese bearing ores.

1.5.3 Objective of the work

Specific problems which have been addressed in the thesis are:

- *Development of a generic flowsheeting approach to analyze the sequential modular flowsheeting using Nagiev's method* [63].

  Grade of ore plays a significant role in deciding the plant's capacity, its operating cost and even in identifying the products to be recovered. So far little attention has been paid during process development studies to the possible changes in cost of metal production when a process plant is exposed to varying degrees of metal grades emanating from a sea nodules mining area. Any process scheme developed for multi metal recovery would need to be assessed from the angle of sensitivity of the proposed scheme to metal throughput and direct chemical costs incurred with input ore grade variation. Modeling of such complex system needs a proper understanding of process and to analyze the performance of the proposed design or plant operation, needs a better way of modeling the whole system is absolute necessity.

- *Development of a generic data driven model for leaching kinetics for reductive leaching of low grade manganese ore.*

  With change of grade, even the kinetics change significantly in the leaching reactor for which process operating conditions including the concentration of leaching and reducing agents get affected. Leaching kinetics of lean ore grades is strongly time dependent and even depends on various other process parameters like concentration of reducing agent, solvent concentration, pulp density etc. Most of the models which have been developed till date do not provide the complete picture of leaching kinetics, so there is a need for development of other modeling techniques which can completely analyze the situation. In this study special attention has been paid to this aspect by constructing data driven models.

- *Process optimization approach involving flowsheeting and data driven kinetic models for reductive leaching of low grade manganese ores.*

  To understand all the aspects regarding performance, process optimization comes handy and most of the real world problems are multi-objective by nature. The optimization of sea nodule treatment flowsheets offers interesting possibilities for process design, where some or all of the associated metals can be recovered. Specifically, a hydrometallurgical flowsheet designed to recover manganese and other associated metals from nodules needs some performance measures. Performance measures like maximization of metal recovery (a combined price function) or maximization of productivity with simultaneous minimization of direct operating cost (chemical consumption) are effectively used in this study.