Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide

Wensheng Zhang *, Chu Yong Cheng

Parker Centre for Integrated Hydrometallurgy Solutions, CSIRO Minerals, PO Box 7229, Karawara, WA 6152, Australia

Abstract

The world rapidly growing demand for manganese has made it increasingly important to develop processes for economical recovery of manganese from low grade manganese ores and other secondary sources. Part I of this review outlines metallurgical processes for manganese production from various resources, particularly focusing on recent developments in direct hydrometallurgical leaching and recovery processes to identify potential sources of manganese and products which can be economically produced.

High grade manganese ores (>40%) are typically processed into suitable metallic alloy forms by pyrometallurgical processes. Low grade manganese ores (<40%) are conventionally processed by pyrometallurgical reductive roasting or melting followed by hydrometallurgical processing for production of chemical manganese dioxide (CMD), electrolytic manganese (EM) or electrolytic manganese dioxide (EMD).

Various direct reductive leaching processes have been studied and developed for processing low manganese ores and ocean manganese nodules, including leaching with ferrous iron, sulfur dioxide, cuprous copper, hydrogen peroxide, nitrous acid, organic reductants, and bio- and electro-reductions. Among these processes, the leaching with cheap sulfur dioxide or ferrous ion is most promising and has been operated in a pilot scale. The crucial issue is the purification of leach liquors and the selective recovery of copper, nickel and cobalt is often difficult from solutions containing soluble iron and manganese. For treatment of manganese bearing materials including waste batteries, spent electrodes, sludges, slags and spent catalysts, a leaching or reductive leaching step is generally needed followed by various purification steps, which makes the processes less economically viable.

It is concluded that the recovery of manganese from nickel laterite process effluents which contain 1–5 g/L Mn offers a growing low cost resource of manganese. Part II of this review considers the application of various solvent extraction reagents and precipitation methods for treating such manganese liquors.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Manganese; Metallurgy; Leaching; Chemical manganese dioxide; Electrolytic manganese dioxide

1. Introduction

Manganese is an important metal in human life and industry. In recent years, the world manganese demand has been driven by soaring steel production, particularly in China. Steelmaking, including its iron making component, has accounted for most of the world manganese consumption, presently in the range of 85% to 90% of the total demand (Corathers, 2004, 2005). Most of the manganese is consumed in steelmaking in the form of manganese ferro-alloys. In 2004, manganese consumption was 60% higher than that of 2003. World production of manganese ore rose steadily by 9% in 2004

and 2005 on a contained-weight basis compared with that in 2004. The price of metallurgical-grade ore (>40%) increased by 16% in 2004 and 63% in 2005 internationally. Combined world production of ferro-manganese and silicomanganese rose by 8% on a gross-weight basis compared with that in previous year (Corathers, 2004, 2005).

The rapid growing demand for manganese metal as an alloying element comes primarily from the alumini-um industry followed by the steel industry and that for electrolytic manganese dioxide (EMD) and chemical manganese dioxide (CMD) come from the primary and secondary battery industries. Industry EMD usage in alkaline batteries in 2002 exceeded 230,000 t per annum with an annual growth rate in excess of 9.6% between 1996 and 2002 (Anon, 2003). Future growth in the EMD market is expected to exceed current growth rates, as global demand for batteries will increase in areas such as mobile communications. A wide range of new products, such as disposable mobile telephone batteries, could see growth rates of up to 8% a year (Anon, 2003). Electrically powered consumer products, from cameras and watches to sophisticated children's games and toys are also an area of robust growth. Extra growth in the demand for EMD is also expected from the secondary or rechargeable battery market as lithium manganese ion batteries (that use EMD in their manufacture) replace cobalt type batteries as the cheaper and more environ-mentally friendly alternative. Growth is also likely to come from the use of EMD in hybrid electric vehicles (HEV's). As the environmental impact of traditional cars continues to cause problems in densely populated cities, the increased usage of HEVs to minimize pol-lution levels seems inevitable.

With the rapid growing demand for manganese prod-ucts, low grade manganese ores (<40%), manganese ocean nodules and secondary manganese sources, which cannot be economically processed by conventional py-rometallurgical processes or pyro-pre-treatment, be-come increasingly important sources of manganese. In recent years, various hydrometallurgical processes have been studied and developed for recovery of manganese from these manganese sources.

In this part of review, conventional pyrometal-lurgical processes and pyro-pre-treatments for produc-tion of major manganese products are briefly outlined. Recent developments in direct hydrometallurgical processes for leaching and recovery of manganese are reviewed in details.

The aims of this part review are to obtain a general knowledge of manganese metallurgy including pyro-metallurgy, pyro-hydrometallurgy and hydrometallurgy and to identify potential sources of manganese and products which can be economically produced.

2. Manganese resources and pyro-processes

2.1. Manganese resources

Manganese is the twelfth most abundant element in the earth's crust (0.096%). Its deposits are generally of sedimentary origin, with oxide ore layers inter-bedded with iron-rich formations (Kaneko et al., 1993). The most common mineral is pyrolusite, which is mainly MnO_2. Manganese is also found in several minerals, such as pink rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$), black manganite ($MnO(OH)$), and alabandite (MnS) (Calvert, 2004). The main sources of manganese come from the former U.S.S.R, Brazil, South Africa, Australia, Gabon and India. Russia and South Africa produce about 85% of the world's pyrolusite.

Manganese nodules or ferro-manganese concretions, usually containing 30–36% Mn, have been found on ocean floors (Calvert, 2004) and could provide another source of manganese. These nodules are found in both the Atlantic and Pacific Oceans, but principally in the Pacific Ocean. Although the primary interests in deep-sea nodules are nickel, copper, and cobalt values, the large quantities of manganese could also be of future importance. As a result, much research work has been devoted to recovering not only nickel, copper and cobalt but also manganese as well.

Manganese bearing materials such as waste batteries and spent electrodes, spent catalysts, steel scraps, sludge and slag are secondary manganese sources. Manganese minerals are often associated with zinc sphalerite ores and nickel laterite ores, which are leached and rejected to the waste effluents in subsequent processing steps. These manganese-containing industrial waste effluents could be potentially important manganese sources. For instance, in the leach solution of the Murrin Murrin Operation of Minara Resources Ltd., the ratio of nickel/ manganese concentrations is in the order of 2:1. Its current nickel production is 36,000 t per annum. Therefore, the manganese in the waste stream is about 18,000 t per annum (Zhang and Cheng, 2006).

2.2. Manganese pyro-metallurgy

Metallurgical grade manganese ores (>40% Mn) are usually processed into suitable metallic alloy forms by pyrometallurgical processes, which are very similar to iron pyrometallurgical processes. Ferro-manganese is a com-monly used alloy. In its production process, a mixture of

manganese ore, reductant (a form of carbon) and flux (CaO) are smelted at above 1200 °C to enable reduction reactions and alloy formation. Standard grade ferromanganese contains more than 76% Mn and about 7% C, and can be produced either in a blast furnace or in an electric furnace (Yucel and Ari, 2001). High carbon ferromanganese can be made by three different practices: blast furnace, discard slag electric furnace, and high manganese slag electric furnace. Medium carbon ferromanganese can be produced by a de-carbonation process or through a redox reaction between silicon in the silicomanganese alloy and manganese ores. Low carbon ferro-manganese is produced by the reaction of manganese ore and low carbon silico-manganese. Silicomanganese is another commonly used alloy, containing 14–16% Si, 65–68% Mn, and about 2% carbon. Lower carbon levels result when the silicon content is increased. Special grades with up to 30% Si are produced for use in the manufacture of stainless steel. The production of silico-manganese is very similar to that of electric smelting of ferro-manganese. It differs in furnace charge which contains large amount of quartz (SiO$_2$) (Yucel and Ari, 2001). Off-grade silicon bearing materials such as ferrosilicon fines, drosses, or ladle dig-outs provide a relatively cheap source of silicon for the silico-manganese making operation because re-melting these materials uses less energy than smelting silicon.

2.3. Manganese pyro-hydrometallurgy

A pyrometallurgical pre-treatment followed by hydrometallurgical processing plays an important role in the treatment of low grade manganese ores and manganese sea nodules containing Ni, Co and Cu values as their oxides. These metal oxides in the nodules often occur in the lattices of iron and manganese minerals. Therefore, breaking up these lattices by pyrometallurgical reduction or hydrometallurgical reductive dissolution is an essential step for the satisfactory recovery of valuable metals. The suggested pyrometallurgical pre-treatments are smelting (Cooper et al., 1959), reduction-roasting (Rolf, 1969), sulphatising (Freitas et al., 1993), and chloridising (Cooper et al., 1959). Compared with pure hydrometallurgical processes, combining pyro-hydrometallurgical treatments yield better results for efficient recovery of Ni, Co, Cu and Mn values from poly-metallic manganese nodules (Kohga et al., 1995), but they require more energy consumption.

In sulphation roasting, the manganese ores or Mn-bearing materials are roasted in the presence of sulfuric acid or ammonium sulfate to convert the manganese minerals to soluble sulfates. Sulphation of manganese ore with gaseous SO$_2$ has been reported (Freitas et al., 1993).

In this case, the gaseous SO$_2$ plays dual roles in the sulphation process: a reductant and a sulphation agent. Sulphation roasting followed by water leaching has been investigated for recycling of zinc-carbon spent batteries with a production of manganese and zinc sulfates (Abbas et al., 1999). The process involves mechanical separation and sulfuric acid leaching, sulphation roasting in the presence of sulfuric acid or ammonium sulfate, followed by water leaching. Maximum manganese recovery efficiency (93.4%) is achieved by using an ammonium sulfate roasting process. In a patented process by Kasimov et al. (1990), the Mn-containing slag, after mixing with (NH$_4$)$_2$SO$_4$, was roasted and then leached with aqueous (NH$_4$)$_2$SO$_4$ to recover manganese compound at low (NH$_4$)$_2$SO$_4$ consumption. The sulfate-containing residue was then pressure-leached at 100–150 °C with aqueous (NH$_4$)$_2$CO$_3$ at a NH$_3$:CO$_2$ mole ratio of 1:1–1.5 and heated to recover (NH$_4$)$_2$SO$_4$ for recycling. This approach for recycling (NH$_4$)$_2$SO$_4$ appears to be expensive involving NH$_3$ input and high pressure leach step, and thus less practical.

Smelting or reduction roasting at about 700–900 °C followed by sulfuric acid leaching is by far the most commonly employed method in the manganese industry for production of intermediate or final manganous sulfate for further electrowinning process (Paixao et al., 1995). The reduction reaction can be presented as:

$$MnO_2 + CO/H_2 \rightarrow MnO + CO_2/H_2O \qquad (1)$$

$$MnO_2 + C \rightarrow MnO + CO(CO_2) \qquad (2)$$

This process converts higher valent manganese oxides to lower ones which are readily soluble in sulfuric acid.

3. Leaching processes

The typical leaching processes involve a chemical reductive step, including bio-leaching and electro-leaching except for acid leaching of Mn(II) ores. Purification, separation and final recovery processes such as solvent extraction, electrolysis and electrowinning, and other recovery processes are then used.

3.1. Reductive leaching with ferrous iron solution

Treatment of manganese ore or manganese bearing slimes with acidified ferrous sulfate or pickle liquors has been reported in several studies (Brantley and Rampacek, 1968; Das et al., 1982; Vu et al., 2005).

A rather novel process for recovery of manganese with pickle liquor (weak FeSO$_4$-H$_2$SO$_4$-(NH$_4$)$_2$SO$_4$
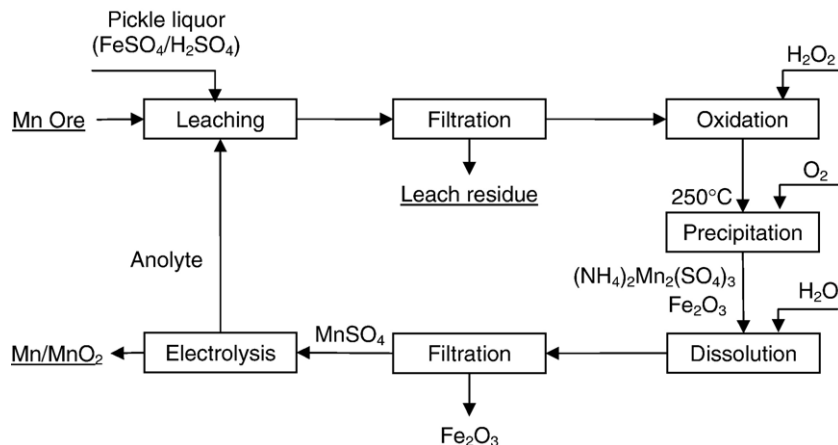
Fig. 1. Flowsheet for the process of Mn recovery using pickle liquor to leach ore (based on Brantley and Rampacek 1968).
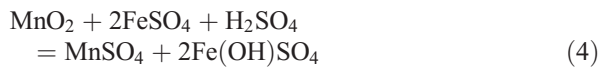
solutions) from low grade manganese ores was developed by US Bureau of Mine (Brantley and Rampacek (1968)). The process is schematically shown in Fig. 1. This process features the simultaneous high temperature hydrolysis of Fe(III) and precipitation of manganese as manganese double salt $(NH_4)_2Mn_2(SO_4)_3$ which is then separated from coprecipitated Fe_2O_3 by dissolution of the salt in water. A relative pure manganese pregnant solution for electrolysis is expected to be obtained in this way. The economical concern of this process is its involvement of expensive H_2O_2 oxidant and a high temperature autoclave process. However, recent developments in pressure oxidation and autoclave technologies may make this approach more attractive.

A study by Das et al. (1982) showed that the reaction of MnO_2 in the low manganese ore with ferrous sulfate could occur in three ways:
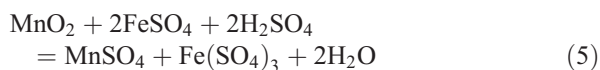
with neutral ferrous sulfate solution

$$MnO_2 + 2FeSO_4 + 2H_2O = MnSO_4 + Fe(OH)SO_4 + Fe(OH)_3 \qquad (3)$$
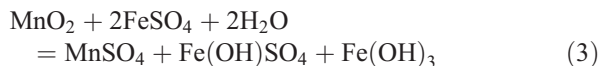
with ferrous sulfate solution and small amount of acid

$$MnO_2 + 2FeSO_4 + H_2SO_4 = MnSO_4 + 2Fe(OH)SO_4 \qquad (4)$$

and with ferrous sulfate solution and excess amount of acid

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe(SO_4)_3 + 2H_2O \qquad (5)$$

More than 90% of manganese could be extracted by leaching the low manganese ore with a stoichiometric amount of ferrous sulfate at 90 °C for 1 h with solid-liquid ratio of 1:10. The leach slurry obtained under the above conditions was gelatinous and difficult to filter. An addition of sulfuric acid made filtration easier and greater Mn extraction, but resulted in 3- 4-fold more iron extraction (Das et al., 1982).
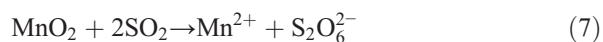
Dundua and Agniashvili (1999) used $FeSO_4$ as leaching agent for manganese recovery from residual slimes in the electrochemical production of manganese dioxide. The resulting liquor was purified by removal of Fe(II) ions using manganese carbonate from low-grade ores. The optimised leaching was proposed for manganese recovery from sludge wastes in the closed-cycle electrochemical production of MnO_2.
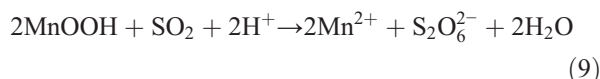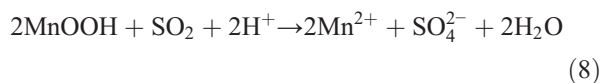
3.2. Reductive leaching with sulfur dioxide or sulfite solutions

Reductive leaching of manganese nodules and low grade manganese oxide ores with SO_2 dioxide or sulfite salts has well been documented in the literature. It is an effective reductant for higher manganese oxide minerals such as MnO_2 and manganese nodules in the hydrometallurgical leaching process. Aqueous SO_2 has been investigated for both percolation and agitation leaching.

Typical studies on leaching of manganese ores with SO_2 or sulfite salts are summarised in Table 1.

The reactions which may occur during leaching manganese oxides are (Petrie, 1995):

$$MnO_2 + SO_2 \rightarrow Mn^{2+} + SO_4^{2-} \qquad (6)$$

$$MnO_2 + 2SO_2 \rightarrow Mn^{2+} + S_2O_6^{2-} \qquad (7)$$

$$2MnOOH + SO_2 + 2H^+ \rightarrow 2Mn^{2+} + SO_4^{2-} + 2H_2O \tag{8}$$

$$2MnOOH + SO_2 + 2H^+ \rightarrow 2Mn^{2+} + S_2O_6^{2-} + 2H_2O \tag{9}$$

The SO_2 is oxidised to SO_4^{2-} and a proportion of dithionate $S_2O_6^{2-}$ by-product depending on solution pH, temperature and redox potentials (Das et al., 1998; Ward et al., 2004; Ward, 2005). A radical mechanism was proposed for formation of dithionate, involving the formation of SO_3 radicals and dimerisation to $S_2O_6^{2-}$ (Petrie, 1995).

In early 1946, a dithionate process was first developed for recovery of manganese from low-grade ores (Ravitz et al., 1946). This is essentially a SO_2 reductive process. The advantage of this process is to utilise the dithionate intermediate product of the reductive reaction to stabilise both the reduced Mn(II) and calcium in solution while extra calcium is precipitated as $CaSO_4$ precipitate. This allows lime to be used as a cheap neutralisation agent. In the semi pilot-plant tests, about 40 runs were carried out on ores assaying 13–18% Mn. Manganese recovery was more than 90% in most cases. A final product containing more than 60% Mn, meeting ferro-grade specifications, was produced. For each unit of manganese extracted, 1.5–2.2 unit of SO_2 and 1.1–1.5 CaO were consumed. The quantity of SO_2 consumed was 60–70% of that introduced.

Dithionate was also used for the treatment of low-grade manganese slimes (Maslenitskii et al., 1969) at a laboratory scale. A recovery of 90% Mn was achieved when the carbonate manganese accounted for 50% of the total manganese content. The manganese content in the produced concentrate was always 55–60%, irrespective of the content in the slimes. The concentrates could be used to produce ferromanganese by the fluxless method or to make electrolytic manganese with the dithionate process.

However, it is generally undesirable to form dithionate in SO_2 leach processes as it requires long residence time to oxidise the dithionate to sulfate and would contaminate the manganese sulfate products by slowly reacting to release sulfur dioxide. A process that minimises the formation of ($S_2O_6^{2-}$) to below 1 g/L by addition of SO_2 continuously at a controlled rate determined by monitoring the solution potential has been developed and reported (Ward et al., 2004; Ward, 2005, see also Section 5.4).

Direct aqueous SO_2 leaching was used for rich Greek manganese ores (Grimanelis et al., 1992). The reaction was found fast with >95% Mn recovery in about 10 min and with low iron impurity. In the studies using low manganese ores (Naik et al., 2000, 2002, 2003), the rate was proposed to be controlled by SO_2 diffusion to the reaction surface, evidenced by a low apparent activation energy of 16.6 kJ/mol. Twice the stoichiometric quantity of SO_2 was required for dissolution of manganese. The $(NH_4)_2SO_3$–bisulfite mixture at the bisulfite/H_2SO_4 (w/w) ratio of 1:(0.52–1.55) was also used as the reductant in leaching the Fe–Mn ore concretions (Sventsitskii et al., 2003; Partenov et al., 2004). The reaction rate was found to be first order with respect to SO_2 concentration and controlled by diffusion of SO_2 to the reaction surface (Partenov et al., 2004).

In processing manganiferrous silver ores where manganese and silver minerals are intimately associated, the reductive leaching by aqueous SO_2 extracts manganese into solution, leaving silver minerals in the residue

Table 1
Reductive leaching of Mn ores/slimes by aqueous SO_2/sulfite

Feed	Reagents	Conditions	Key results	Ref
MnO_2 minerals	Aq. SO_2	Studied leaching chemistry	Sulfate/dithionate ratio depends on pH, Eh and Tem.	Petrie 1995 Das et al. 1998
Rich Mn ore (>40% Mn)	Aq. SO_2	Atm. pressure and room temp.	>95% Mn in 10 min	Grimanelis et al. 1992
Low Mn ore (<40% Mn)	Dithionate	Lime for neutralisation	>60% Mn, meeting ferro-manganese	Ravitz et al. 1946
	Aq. SO_2	Atm. pressure and room temp.	Rapid leaching rate 95% Mn recovery	Naik et al. 2000; 2003
	Aq. SO_2	<60 °C controlled Eh for adding SO_2	Minimised dithionate to 1 g/L	Ward et al., 2004; Ward 2005
Low Mn slimes	Dithionate	–	90% Mn recovery 55–60% Mn content	Maslenitskii et al. 1969
Fe–Mn concretions	$(NH_4)_2SO_3$–bisulfite–H_2SO_4	pH 3.5–5.5 30–70 °C	96% Mn recovery	Sventsitskii et al. 2003
	Aq. SO_2	Kinetic study	E =16,6 kJ/mol SO_2 diffusion control First order: [SO_2]	Partenov et al. 2004
Low Mn ores (Percolation)	Aq. SO_2	Size 1.3–2.5 cm 1.5%-sat. [SO_2] 15–20 days	Rate depends on [SO_2] and pH >90% Mn recovery	Abbruzzese 1987 Pahlman and Khalafalla 1988 Abbruzzese 1990

which could be recovered by subsequent cyanidation (Pahlman et al., 1987).

In percolation (Abbruzzese, 1990), the extent of the extraction depends mainly on the dissolved SO_2 concentration and the acidity of the leach solution, which govern the thermodynamic conditions of the system. The pH must be maintained below the pK_a and the concentration of SO_2 around the saturation value (6%). Ambient temperature and small particle size favour manganese recovery. The maximum extraction was achieved in 15–20 days of leaching. Simultaneous dissolution of iron was found to be significant when the ore contained goethite and siderite. Dissolution of calcium could be inhibited by low flow rate of the leach solution. Over 90% Mn recovery could be achieved (Pahlman and Khalafalla, 1988). Pilot percolation plant leaching tests (Abbruzzese 1987) showed that total manganese recovery was 94.4% which was slightly lower than values obtained in the batch tests. The pregnant solution of $MnSO_4$ containing mainly Fe and Zn impurities was purified using 20% DEHPA in kerosene for extraction of Fe(III) at pH 1.5–1.8 and Zn at pH 4. The main concerns on the application of the aqueous SO_2 for leaching of manganese ores in percolation is the control of SO_2 and the acidity, which appear difficult and costly.

3.3. Reductive leaching with organic reductants

Many studies have focused on reductive leaching of manganiferrous ores containing tetravalent manganese using organic reductants, including sawdust (Sanigok and Bayramoglu 1988), glucose, sucrose (Veglio and Toro 1994a,b), lactose (Ali et al., 2002 Ismail et al., 2004), glycerine (Arsent'ev et al., 1991), oxalic acid,

citric acid, tartaric acid, formic acid (Sahoo et al., 2001; Rodriguez et al., 2004), and triethanolamine and thiosulfate (Yavorskaya et al., 1992). The conditions and main results are summarised in Table 2.

The carbohydrate reductants are considered to be cost effective and non-hazardous, which may be used either in pure form or from industrial wastes (Veglio and Toro 1994a,b). The stoichiometry was proposed as follows.

$$C_6H_{12}O_6 + 12MnO_2 + 24H^+ \\ = 6CO_2 + 12Mn^{2+} + 18H_2O \qquad (10)$$
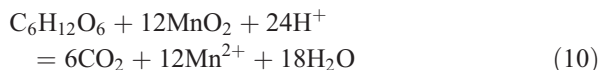
The reaction products of the glucose were identified using HPLC (Furlani et al., 2006). In sulfuric acid medium, the glucose was oxidized via formation of monocarboxylic polyhydroxyacids and formic acid. Formic acid was identified and quantified as the major component. Poly-hydroxyacids, especially glyceric and glycolic acid, were found in minor quantities together with traces of gluconic acid.

Sawdust and oxalic acid are also of interest to industrial applications due to its cheap cost and availability.

3.4. Bio-reductive leaching

In addition to the studies on chemical leaching processes, a certain emphasis has been placed on reductive biological treatment that generally uses heterotrophic microorganisms (Abbruzzese et al., 1990; Veglio et al., 1997). The mechanism can be direct and indirect. In direct leaching mechanism, the bacteria are capable of utilizing the MnO_2 as a final acceptor of electrons in the

Table 2
Reductive leaching by organic reductants

Reductant	Ore	Conditions	Key Results	References
Glucose	Mn nodules	2.5 M NH_3, 0.37 M NH_4Cl, 0.2 g glucose/g of nodules, 85 °C, 4 h	(%) Cu 100, Ni 90, Co 60	Das et al. 1986
Sawdust $(C_6H_{10}O_5)_n$	Low Mn Ore	Aq. H_2SO_4	90–95% Mn (99.6% pure)	Sanigok and Bayramoglu 1988
Sucrose $(C_{12}H_{24}O_{11})$	Pyrolusite	50–90 °C 20 g/L of sucrose H_2SO_4: Mineral=0.98 Sucrose:Mineral=0.1	94–95% Mn recovery	Veglio and Toro 1994a; 1994b
Lactose $(C_{12}H_{22}O_{11})$	Low Mn Ore	100 mesh, 2 h, 90 °C H_2SO_4/ MnO_2 =1.8 lactose/Mn-ore=0.75	90–92% Mn recovery	Ali et al. 2002 Ismail et al. 2004
	Mn–Ag Ores	Two stage leach with H_2SO_4 and then thiourea	97% Mn 98% Ag and Au	Ziyadanogullari and Buyuksahin 1995
Glycerine	Mn ores	Aq. H_2SO_4 glycerine/MnO_2=(1–2.5)	Increased Mn recovery	Arsent'ev et al. 1991
Triethanolamine and Thiosulfate	MnO_2	H_2SO_4:Mn <2.6 Thiosulfate/ MnO_2=(0.25–0.28)	Maximum Mn recovery	Yavorskaya et al. 1992
Oxalic Acid (OX)	Low Mn Ore	30.6 g/l OX, 0.5 M H_2SO_4 85 °C, 105 min.	98.4% Mn recovery	Sahoo et al. 2001
Carboxylic Acid (15%) HF (9%)	Ferro columbite	HF+tartaric (TR), citric, formic, oxalic (OX) acids	TR increases %Fe and Mn OX decreases %Mn	Rodriguez et al. 2004

respiratory chain of their metabolism, instead of oxygen. In the indirect mechanism, the reductive process is associated with the formation of reductive compounds, resulting from their metabolism. In all cases, the biological process occurs in the presence of organic carbon and energy sources.

The mechanism of the bioleaching was found to be predominantly indirect through the production of organic acids, mainly oxalic acid and citric acid in the leaching medium which reduced manganese oxides (Acharya et al., 2003). Oxalic acid is potentially of greater interest than citric acid due to its reductive activity for MnO_2 according to the following reaction (Abbruzzese et al., 1990):

$$MnO_2 + 2H^+ + C_2O_4H_2 = Mn^{2+} + 2\,CO_2 + 2H_2O$$

$$(11)$$
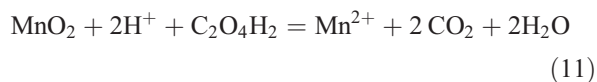
The manganese ions (released as manganese oxalate and manganese citrate) formed a product layer on the ore, and the reaction was proposed to be controlled by diffusion of the reactants through the permeable product layer (Acharya et al., 2003). The kinetic equation could be expressed by the shrinking core model $[1-(1-\alpha)^{1/3}]^2$ kt (where α is the fraction of manganese reacted, k the rate constant and t the reaction time) (Acharya et al., 2003).

Acharya et al. (2001) investigated microbial extraction of manganese from the low grade manganese ore which was collected from Joda East manganese mines of Orissa. The microorganism used was an indigenous fungal culture, *Penicillium citrinum,* isolated from the top soil of the same mines. An extraction of 64% manganese was obtained within 30 days.
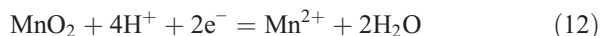
Research workers in Greece and Italy (Veglio et al. 1997) investigated a batch and semi-continuous process for bioleaching of manganiferous minerals with heterotrophic mixed microorganisms. 95–100% of manganese extraction could be obtained in 36–48 h of treatment using a content of pulp containing 20% (w/v) of ore having a Mn grade of 17–20%. Final tests in a pilot plant (V=70 L) were performed under non-sterilised conditions. The experimental results showed a technical feasibility of the process although several problems have to be resolved to allow for a full-scale application, such as the biomass disposal, the purification of the leach liquor before the final manganese recovery, and the high cost of the process.

3.5. Electro- reductive leaching

Electro-leaching dissolves the manganese minerals in leach solutions whose potential is controlled potentios-

tatically. This method is based on the principle that manganese dioxide can be used as an electrode because it is a semi-conductor. In the electroslurry process, manganese is cathodically dissolved from oxide slurry by direct electroreduction.

Elsherief (2000) has recently applied electro-reductive leaching for upgrading Egyptian low-grade manganese ores in sulfuric acid solutions using a slurry electrolysis cell. It was found that MnO became readily soluble in acid under reductive conditions. Cyclic voltametric studies on carbon paste electrodes of the ore and its mineral constituents showed that maximum reduction of manganese occurred at 0 mV with respect to a mercury/mercurous sulfate reference electrode. The acid concentration, the reaction temperature, and the applied potential affected the reaction rate and level of extraction of manganese from the ore. The rate of reduction increased with increasing acidity. The reactions were proposed as follows:

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \qquad (12)$$

$$MnO_2 + H^+ + e^- = MnOOH \qquad (13)$$

$$MnOOH + 3H^+ + e^- = Mn^{2+} + 2H_2O \qquad (14)$$

With sufficient accumulation of MnOOH on the surface of the MnO_2, further reduction to $Mn(OH)_2$ could occur:

$$MnOOH + H^- + e^- = Mn(OH)_2 \qquad (15)$$
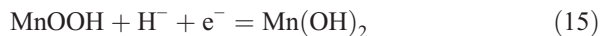
The presence of Fe^{2+} and Mn^{2+} ions greatly increased the speed of reaction. This could be due to an involvement of Fe^{2+} in the chemically reductive reactions as shown in reactions (3–5). Temperature was found to have a major influence on the leaching process. The main reduction process resulted in Mn^{2+} release and selectivity could be achieved. At 20 °C, very poor recoveries of metals were recorded. Under optimum conditions at 70 °C in 50 g/L H_2SO_4 solutions at 0 mV, manganese was fully extracted whereas 56% iron was extracted in 45 minute electrolysis. The amount of manganese leached by the electrolysis at 0 mV was approximately five times more than that recovered by chemical leaching without applied potential.

3.6. Simultaneous leaching manganese(IV) oxide and sulfide minerals

Many studies have been carried out to leach manganese oxides and sulfide minerals simultaneously in an acid medium, H_2SO_4 or HCl. In this leaching process, the

Table 3
Simultaneous leaching of Mn oxides and metal sulfide minerals

Sulfides	Mn oxides	Conditions	Key results	Ref
Pyrite (FeS_2)	Low Mn ore	H_2SO_4, 175 °C (1) with O_2 (2) without O_2	(1) $MnSO_4.H_2O$ product (2) $FeSO_4$ suitable for leaching at room temp	Thomas and Whalley 1958
	Mn ore	10% H_2SO_4 Mn:pyrite ore=1:1	milled before leaching increased Mn recovery	Gaprindashvili et al. 1993
	Mn Conc. (58% MnO_2)	10% H_2SO_4 85–95 °C	99% Mn recovery	Omarov and Beisembaev 1996
	Mn–Ag ores	Residue cyanidation	93% Mn recovery 92% Ag recovery	Lu and Zou 2001
ZnS	MnO_2	H_2SO_4 sol.	$MnSO_4$, $ZnSO_4$ suitable for electrowinning	Li 2000
	Mn–Ag ores	H_2SO_4 sol. Ag by NH_3 leach	98% Mn recovery 92% Ag (99% pure)	Yaozhong 2004
FeS_2/ZnS/PbS	Mn ore	H_2SO_4 sol.	Key factor: MnO_x:MeS, Temp.	Kholmogorov et al. 1998
Ni matte	Mn nodules	1.5–2.0 M HCl 95 °C, 80 min	>90% Ni and Cu and 80% Co	Chen et al. 1992
Zn matte	Mn nodules	HCl solution, 70 °C	97% Mn, 92% Co, and 88% Ni	Kuh et al. 2001
Pyriti-ferrous lignite	Low Mn ore	1.9 M H_2SO_4 Ore/lignite= 1:1.8 99 °C, 3 h	>99% Mn recovery	Naik et al. 2002

sulfide minerals function as reductants while the manganese oxides as oxidants. The sulfide minerals include galena (PbS) (Kholmogorov et al., 1998), sphalerite (ZnS) (Kholmogorov et al., 1998; Li, 2000; Yaozhong, 2004) or zinc matt (Li, 2000), pyrite (FeS_2) (Thomas and Whalley, 1958; Gaprindashvili et al., 1993; Omarov and Beisembaev, 1996; Kholmogorov et al., 1998; Lu and Zou, 2001), nickel matte (Li, 2000), pyriti-ferrous lignite (Naik et al., 2002). The key operation parameters were found to be the MnO_x:MeS ratio, acid concentration, temperature and leach time (Kholmogorov et al., 1998). The leach conditions and major results are summarised in Table 3.

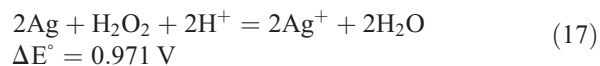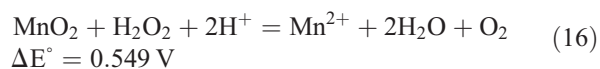Among the sulfides, pyrite concentrate offers some advantages:

1. The iron introduced can be easily removed as iron oxides or hydroxides in the presence of oxygen.
2. In the absence of oxygen, Fe(II) can be used as a reductant in subsequent leaching process.

Other valuable metal sulfides such as nickel and zinc can only be justified for special cases, e.g. a comprehensive recovery of these metal values from polymetallic manganese nodules.

3.7. Leaching with hydrogen peroxide

Jiang et al. (2003) investigated a simultaneous leaching process for extraction of manganese and silver by one-step leaching in sulfuric acid solution in the presence of hydrogen peroxide. Thermodynamics of the Mn–H_2O and Ag–H_2O systems show that there is a predominance region where Mn^{2+} and Ag^+ coexist in solution. Hydrogen peroxide plays dual roles in the process: as an oxidizing agent for native silver and a reducing agent for manganese dioxide based on the following reactions:

$$MnO_2 + H_2O_2 + 2H^+ = Mn^{2+} + 2H_2O + O_2 \qquad (16)$$
$$\Delta E° = 0.549 \text{ V}$$

$$2Ag + H_2O_2 + 2H^+ = 2Ag^+ + 2H_2O \qquad (17)$$
$$\Delta E° = 0.971 \text{ V}$$

A recovery of 98% for manganese and 85% for silver was attained for an ore analysing 12.2% Mn and 1850 g/t Ag under the conditions of 0.8 mol/L H_2O_2, 0.8 mol/L H_2SO_4, 25 °C, and 2 h of residence time.

3.8. Leaching with hydrochloric acid solution

A hydrochloric acid leaching process for manganese recovery from manganese ores has been proposed and patented by Abdrashitov et al. (2001). In this process, the Mn-ore feed was leached with aqueous 5–20% HCl solution, which resulted in the associated evolution of Cl_2 and the formation of $MnCl_2$. The leach solution together with $MnCl_2$ and Cl_2 was treated in the subsequent stage by addition of Na_2CO_3 to precipitate purified MnO_2 product in the presence of aqueous NaCl and evolved CO_2. The typical manganese recovery into solution by the acidic leaching was 97.0% at 101.6 g/L Mn, and the MnO_2 precipitate in the second stage was 98.0% pure compared with 17–50% Mn and 50% SiO_2 in the ore feed. The novelty of the invented process utilises the chloride ions as the reductant at high acidity and the Cl_2 product as the oxidant to precipitate the reduced manganese as MnO_2 in alkaline conditions. However, this process is expected to be rather expensive

and inefficient because a very high acidic condition is needed for the chloride ions to function as a reductant. In addition, the corrosive Cl_2 gas has to be collected and to be used in the subsequent precipitation step.

3.9. Leaching with nitrogen dioxide and nitric acid solutions

A nitrous-nitric process was developed for recovery of manganese from manganese ores by Dean et al. (1942) at U. S. Bureau of Mines. The process involved leaching the ore with NO_2 and decomposing the resulting $Mn(NO_3)_2$ solution. Five hours of nitration of Cuyuna Merritt ore (−65 mesh) gave at least 95% extraction of manganese in a solution low in iron and phosphate. HNO_3 formation could be maintained as low as 0.3 g per gram of manganese by controlling the NO_2 flow and eliminating air pressure. Manganese concentrations of 300 g/L could be obtained. Evaporation of the pregnant liquor resulted in quantitative precipitation of Fe and P. Electrolytic decomposition of the filtered solution, heated by alternative current, proved to be the best method to decompose the salt and gave a high-purity MnO_2. Magnesium nitrates could be removed by bleeding and re-crystallisation.

In a recent development by Drinkard and Woerner (1997), HNO_3 has been used in leaching for recovery of metal values from metallurgical dust wastes. Although

nitrous-nitric process is effective, HNO_3 is an expensive reagent and the resulting effluent is difficult to treat.

3.10. Acid leaching of Mn(II) carbonate and silicate ores and slags

Manganese carbonate and silicate minerals are soluble in acids, e.g., in sulfuric and hydrochloric acids. Several acid leaching processes have been developed to recover manganese from these kinds of manganese minerals.

Arsent'ev et al. (1992) investigated hydrometallurgical methods for processing of Vorkutinsk manganese ores. The ores containing 41.1% Mn consisting of 53–55% carbonates and 40–43% silicates were ground and leached with H_2SO_4 (0.8 kg/kg ore) for 1.5 h at above 90% Mn recovery. The leach solution was then neutralized, and a carbonate concentrate was produced, containing 35–45 Mn and 0.2% SiO_2 at 98% removal.

Das et al. (1978, 1979) investigated the recovery of manganese from ferro-manganese slag by acid leaching. The slag from ferro-manganese manufacture contained 12–30% Mn(II) with the main impurities being CaO, SiO_2, and Al_2O_3. The slag was leached with HCl or H_2SO_4. Manganese recovery was over 90% under optimum conditions.

Comba et al. (1991) developed a calcium fluoride-enhanced hydrochloric acid leaching procedure for

Table 4
Reductive leaching of manganese nodules by aqueous SO_2/sulfite

Reagents	Conditions	Key results	Ref
$(NH_4)_2SO_3$ (S1) $(NH_4)_2CO_3$ (S2)	−100 mesh 80 °C, 120 min 50 g/L (S1) 120 g/L (S2)	S1 enhanced recovery (%) Ni 93, Co 98, Cu 97 Mn and Fe<1	Maslenitskii et al. 1969
SO_2–H_2SO_4	Control the ratio of mole of SO_2 to nodule weight	Selective for Ni, Co, and Mn over Fe and Cu	Pahlman and Khalafalla 1979; Kanungo and Das 1988
SO_2 SO_2–NH_3		SO_2 alone non-selective SO_2–NH_3 selective for Ni, Co, and Cu	Kawahara et al. 1991
SO_2–NH_3 (Pressure leach)	Pilot plant pH 8–9	(%) 85 Cu, 90 Ni, 80 Co 55% Mn in Mn cake	Mittal and Sen 2003
$(NH_4)_2SO_3$	80–110 °C	Ea=62 kJ/mol R=k[S(IV)][MnO_2]$^{0.5}$ Fit $1-(1-a)^{1/3}$ =kt	Das et al. 1998 Demirbas 1999
SO_2(a)–H_2SO_4 (b)–$(NH_4)_2SO_4$(c)	60 g/L (a), 3% (b), 100 g/L (c) 20% solid, 3 h	(%) 88.5 Cu, 99.8 Ni, 91.8 Co, 97.8 Zn, 99.6 Mn and 2.4 Fe	Acharya et al. 1999
Na_2SO_3–$(NH_4)Cl$	10–80 °C 0.5–2.5 h	R depends on [S1] and [S1] R$_{(Mn,\ Ni,\ and\ Cu)}$ pore diffusion R$_{(Fe)}$ surface chemical Rate $_{(Co)}$ jointly controlled	Choi et al. 1996 Li et al. 1997 Sventsitskii et al. 2003
(1) spent electrolyte (2) 100 g/L $FeSO_4$	(1) 40–80 °C (2) 50 °C, pH 3–4	(1) leach Ni and Cu (2) leach Co and Mn	Kane and Cardwell 1976
$FeSO_4$–H_2SO_4	90 °C, 30 min	>90% Ni, Cu and Mn >85% Co	Vu et al. 2005
Roasting NH_3/Air leach	Roasted at 750 °C Two stage leaching	(1) monitor Eh for Co recovery (2) selective for Ni and Cu	Jana et al. 1999
Roasting NH_3–CO_2 leach	190–200 NH_3 85–110 g/L CO_2 Leachate aeration	51–57% Mn recovery	Javorek 1988
Roasting aq. NH_3–$(NH_4)_2CO_3$	Leach with air	Selective (%) 93 Ni, 92 Cu, 65 Co	Saha et al. 1993

recovery of manganese from manganese-bearing silicate ores. The proposed process is an alternative to high-temperature and energy-intensive extractive techniques. Single-stage leaching with a stoichiometric amount of HCl and F-Mn mole ratio of 0.2 extracted 96% Mn when the leaching conditions were 50 °C, 3 h, and 35% solids. Manganese at 98% recovery was achieved during a countercurrent leaching under similar conditions and 99% CaF_2 was reclaimed.

4. Processing of manganese nodules, heterogenite and secondary materials
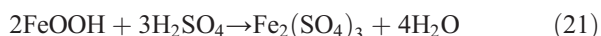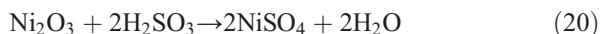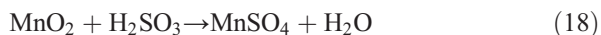
4.1. Processing of manganese nodules

Manganese nodules have been recognized as a potential source of various metals such as Cu, Ni, Co and Mn. It is well known that the manganese nodules contain these metals as higher oxides or hydroxides and usually amorphous in nature. Therefore, it is essential to roast or leach the manganese nodules in the presence of a reductant. In pre-roasting, non-coking coal can be used as reductant followed by leaching (Javorek, 1988; Saha et al 1993). In direct reductive leaching, various reductants were investigated including sulfur (Mohanty et al., 1994), SO_2 or sulfurous acid (Pahlman and Khalafalla, 1979; Kanungo and Das, 1988), manganous ion (Acharya and Das, 1987), glucose (Das et al., 1986), Charcoal (Das et al., 1989) and ferrous iron (Anand et al., 1988). Among these reductants, SO_2 and $FeSO_4$ are two of the effective reductants for MnO_2 leaching. However, SO_2 is preferred for its rapid rate of reaction, low temperature operation, ease of purifying leach liquor and elimination of barren solution disposal problem. Importantly, SO_2 is cheap to make and can be easily extracted from spent gas of smelters.

In comparison to manganese ores, the leaching of manganese nodules is more complex and difficult due to their matrix structures and polymetallic value recoveries. These metals are present in nodules as oxides or hydroxides. The major matrices for Mn and Fe are todorokite (buserite), δ–MnO_2, goethite, maghemite or Mn-hematite, where nickel and copper are mainly associated with manganese oxide phases and cobalt mostly with the iron phase, but possibly also with the manganese oxides. The most stable species of these elements in the ocean environment are MnO_2, Fe_2O_3, CuO, Ni_3O_4 and Co_2O_3 (Vu et al., 2005). The recent developments in processing ocean manganese nodules have been reviewed by Mukherjee et al. (2004). Table 4 summarises typical studies on reductive leaching of manganese nodules.

4.1.1. Leaching with sulfur dioxide

The higher oxides of Mn Ni and Co in manganese nodules, if present, would require reductant to convert the higher oxides to soluble forms. Goethite may give ferric sulfate or is reduced to give ferrous sulfate in solution. The various reactions in the presence of aqueous SO_2 have been reported by Acharya et al. (1999):

$$MnO_2 + H_2SO_3 \rightarrow MnSO_4 + H_2O \tag{18}$$

$$Co_2O_3 + 2H_2SO_3 \rightarrow 2CoSO_4 + 2H_2O \tag{19}$$

$$Ni_2O_3 + 2H_2SO_3 \rightarrow 2NiSO_4 + 2H_2O \tag{20}$$

$$2FeOOH + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 4H_2O \tag{21}$$

$$2FeOOH + H_2SO_4 + H_2SO_3 \rightarrow 2FeSO_4 + 3H_2O \tag{22}$$

The selectivity of Ni, Co and Mn over Cu, Fe and Al was found to depend on the ratio of the mole of actually dissolved SO_2 in the solution (M_{SO2}) to the weight of ground nodules (W_{sn}) (Pahlman and Khalafalla, 1979). Optimum ratio of Mn_{SO2}/M_{sn} would vary with specific composition and amount of nodules. For the Indian Ocean nodules which are low in copper, such selective leaching may not be economically viable (Kanungo and Das, 1988).

Depending on the reaction conditions, formation of manganese dithionate or soluble metal bisulfites may take place. The Fe(III) present in the solution may precipitate as jarosite in the presence of ammonium sulfate as shown below:

$$\begin{aligned} 3Fe_2(SO_4)_3 + 12H_2O \\ + (NH_4)_2SO_4 \rightarrow 2NH_4Fe_2(SO_4)_3(OH)_6 \end{aligned} \tag{23}$$
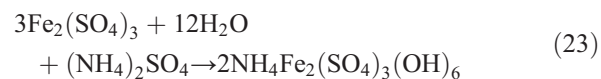
The rate of leaching with aqueous SO_2 was found to increase with dissolved SO_2 concentration up to 80 °C (Demirbas, 1999). In the temperature range of 80–100 °C, the activation energy was determined to be 62–65 kJ/mol, indicating a chemically controlled process (Das et al., 1998; Demirbas, 1999). In sodium sulfite and NH_4Cl solution, the dissolution rates of manganese, nickel and copper were found to be controlled by pore diffusion, whereas iron by surface chemical reactions and cobalt limited by both surface chemical reactions and pore diffusion (Choi et al., 1996). With an increase in temperature from 80 to 100 °C, the ratio of Mn^{2+}/Mn^{3+} increased by about five times indicating favourable formation of lower valency states of manganese ions at higher temperatures (Das et al., 1998). Similar to the leaching of manganese ores, the reaction product of SO_2 was mainly sulfate with a

proportion of dithionate ($S_2O_6^{2-}$), depending on specific leach conditions (Popov et al., 1981). The ratio of dithionate to sulfate was found to increase with increasing SO_2 concentration and higher solution pH in the leach solution.

For processing polymetallic values such as Ni, Co, Cu, Mn, and Fe, the leaching with aqueous SO_2 alone was found to be non-selective (Kawahara et al., 1991; Li et al., 1997). A selective extraction of Ni, Co, and Cu from Mn nodules can be achieved by using ammonia/carbonate solution in the presence of sulfur dioxide as the reductant. Strategies in the presence and absence of O_2 (air) can be used to selectively complex metal values in the solution or to precipitate basic manganese carbonate via heating and recovery of ammonia (Rokukawa 1990). Pre-treatment of the ores with dilute acetic solution was found to be effective to remove a substantial quantity of calcareous and carbonaceous material from the nodules (Pahlman and Khalafalla, 1988). An increase in temperature suppressed the dissolution of iron into the leach solution. The leaching residue was mainly composed of manganese ammonium sulfite hydroxide ((NH_4)$_2Mn_2(SO_3)_3$) in an ammonia solution while manganese carbonate was detected in the leaching with ammonium carbonate solution. Most of Cu, Ni, and Co was extracted into solutions, leaving most manganese in the residue at 80 °C for 120 min.

A polymetallic manganese nodules pilot plant of 500 kg per day processing capacity was designed and set up at Hindustan Zinc Limited, Udaipur (India) (Mittal and Sen, 2003). The process was based on the reductive alkaline pressure leaching of nodules using sulfur dioxide as reducing agent in the presence of ammonia at pH 8–9. The overall process scheme is shown in Fig. 2.

In this process, the partially dissolved manganese during leaching along with copper, nickel and cobalt was precipitated and separated out as manganese dioxide in a demanganisation autoclave by sparging oxygen. Free ammonia present in the leach liquor was recovered in an ammonia stripper and recycled back to leach autoclave as recycled ammonia. Ammonia free leach liquor was subjected to single stage copper extraction with LIX 84I at controlled pH for selective removal of copper. The copper raffinate containing dissolved nickel and cobalt was subjected to sulfide precipitation using sodium sulfide. The nickel and cobalt were precipitated as sulfides along with minor impurities like copper, zinc, iron etc. The cake was dissolved in a dilute sulfuric acid solution in the presence of oxygen under medium temperature and pressure conditions. The cobalt and nickel in the purified leach solution were extracted with PC-88A and D2EHPA respectively and produced as pure metal through electro-winning. The experiments conducted in the pilot plant showed an average recovery for copper, nickel and cobalt as 85%, 90% and 80%, respectively.

The process has several advantages and compares well with other alternative hydrometallurgical processes for extraction of metals from poly-metallic nodules. First, the major reagent is sulfur dioxide, which is comparatively cheap and can also be economically extracted from smelter off-gases. Second, the high recoveries for nickel, copper and cobalt values can be achieved, which not only covers the mining cost but gain additional profits. Last, the manganese cake containing 55% manganese can directly be used for the production of high-grade ferro-manganese.
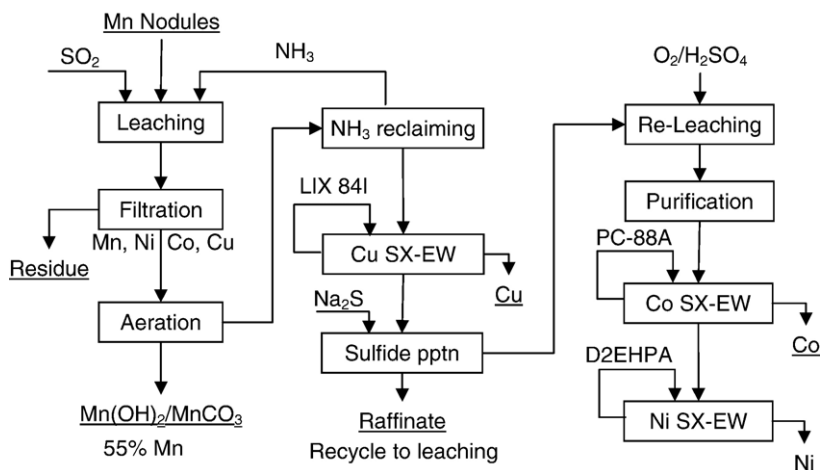

Fig. 2. Schematic flowsheet of manganese nodule pilot operation using SO_2 reductant in Indian (based on Mittal and Sen 2003).

The National Metallurgical Laboratory (NML) of India developed a two stage ammoniacal leaching scheme with a prior pre-conditioning step (Jana et al., 1999). The necessity of monitoring redox potential in the first stage leaching to control cobalt recovery has been emphasized. Based on the two stage leaching scheme, recycle leaching has been carried out to generate leach liquor having suitable composition for the subsequent solvent extraction-electrowinning operation. The average recovery of metals in 16 cycles of leaching has been found to be 92% Cu, 90% Ni and 56% Co.

4.1.2. Leaching with $FeSO_4$

A two-stage leaching process for selectively extracting metal values from manganese nodule was developed by Kane and Cardwell (1976). In the first stage leaching, spent electrolytes containing about 4% free acid were used to leach the nodule for 14 h at 40–80 °C for preferentially extracting nickel and copper values. In the second stage, the filtered solids were reductively leached with solutions containing approximately 100 g/L $FeSO_4$ at about 50 °C and pH 3–4 to extract cobalt and manganese. Air was bubbled through the leach solution in the second stage to remove iron as oxides/hydroxides to the residue. Copper was extracted at pH 2 from the first stage leach solution using a α-hydroxy oxime or 8-hydroxyquinoline. The copper strip solution was electrolysed to give the cathodic copper product, and the raffinate from the solvent extraction was similarly treated in a nickel cell for the recovery of cathodic nickel. After iron was removed from the second leach solution, cobalt was extracted by the organic solution at pH 3.5–4.5, and the raffinate was electrolysed for the recovery of manganese.

Leaching of manganese nodule in ammoniacal medium using $FeSO_4$ as the reductant was investigated by Anand et al. (1988). Ferrous iron in ammonia-ammonium solution can form a sable ferrous ammine complex in the pH range of 9.5 to 9.8. It is oxidised and precipitated as ferric hydroxide by simultaneous reduction of MnO_2, Ni_3O_4, Co_2O_3 minerals to lower-valence metal ions which can be stabilised in the solution as metal ammines. While maintaining the total molarity of ammonia and ammonium sulfate at 5.85 M, most of the copper, nickel and cobalt, and about 32% of manganese could be leached within 10 min. An extension of leach time resulted in partial precipitation of manganous ammine as MnO or Mn_2O_3 and the loss of nickel and cobalt due to coprecipitation or adsorption. This process could eliminate iron in the solution in the ppm level. However, it was difficult to optimise the selectivity of Ni, Co and Cu over manganese by varying the total concentration of

ammonia and ammonium sulfate in the range of 1.96 to 5.85 M. Other variable affecting the extent of extraction of Ni, Co, Cu and Mn included the amount of ferrous sulfate, leaching temperature and initial pH.

More recently, the leaching of manganese nodule with $FeSO_4$–H_2SO_4–H_2O solutions has been reported (Vu et al., 2005). The manganese deep ocean nodules originated from the IOM area, located in the Clarion–Clipperton ore field. The optimum conditions established were as follows: stoichiometric amount of $FeSO_4$, 1.6-fold excess over stoichiometric amount of H_2SO_4, 90 °C, l/s of 7:1, grain size ≤ 1000 μm. Under these conditions, more than 85% of Co and 90% of Ni, Cu and Mn could be extracted within 30 min. The leach liquors contained approximately 146 mg/L Co, 1.63 g Ni/L, 1.69 g Cu/L and 30 g/L Mn.

Compared with a non-selective leaching process, the two-stage leach process enable nickel to be separated from cobalt at early leaching stages and make the subsequent separation process simple and easy, but the energy consumption is expected to be high in the leaching stages. The applicability of the process would largely depend on the valuable metal grades in the nodules and the availability of cheap spent industrial pickle liquors.

4.1.3. Leaching with nitrogen dioxide and nitric acid

Nitrous-nitric method was tested for processing ocean nodules to recover the manganese value selectively (Welsh and Sochol, 1978). The nodules comprised primarily oxides of manganese and iron with lesser amounts of Cu, Ni, Co, alkali metal and alkaline earth metal compounds. The process was comprised of leaching the nodules at 80 °C with an aqueous solution of nitrous and nitric acids; removing insoluble iron oxide and gangue at pH <2.5 by filtration, adding Mn$(OH)_2$ to the filtrate to selectively precipitate Cu, Ni and Co metals as hydroxides and adding to the filtrate H_2S to precipitate metal traces as sulfides to obtain purified manganese sulfate solution.

4.1.4. Leaching with cuprous copper solution

Szabo (1976) developed an ammoniacal cuprous leach process for recovery of metal values from manganese deep sea nodules. This process has been tried at a pilot plant. The process consisted of ore preparation, reduction-leach, oxidation and wash-leach, LIX separation of the metals, and electrowinning. The nodules were leached with an ammoniacal solution containing Cu(I) ions to reduce the manganese oxides and extract Cu, Ni, Co and Mo into solution. The cuprous ions used for the leaching were regenerated by reduction of the Cu(II) with a reducing gas such as a mixture of CO 95%

and H_2 5%. The nodule residue was washed with an ammoniacal-$(NH_4)_2CO_3$ solution to remove entrained metal values and the wash effluent contained Cu, Ni, Co, and Mo values. Rappas (1985) reported a process for the extraction of metals from laterite ores and ocean manganese nodules with a stabilised acidic cuprous ion solution (Cu^+L) in a suitable reactor at a temperature up to 90 °C and pH in the range of 1.5–2.5, wherein L is a stabilising ligand selected from the group consisting of CO, XRCN and Cl^-, X being H or OH and R being aliphatic compound having 1–4 carbon atoms.

The cuprous copper process is considered less suitable for practical applications due to the unstable nature of the cuprous ions in the leach solutions. Sufficient ligands or complexing agents are needed to present in the leach solution and also in the relatively expensive regeneration process.

4.2. Treatment of heterogenite

In recent years a new manganese bearing ore has drawn attention. It is heterogenite from Africa, containing cobalt, cupper and significant quantities of manganese. A frowsheet was developed and piloted at Mintek during 1998 for recovering Cu and Co from the Kakanda (Democratic Republic of Congo) tailings (Dry et al., 1998; Sole et al., 2005). This was an acid/SO_2 reductive leaching process. Copper in the leach solution was recovered by SX-EW. A bleed of the raffinate went through Fe and Al removal by neutralisation, manganese (about 1 g/L) recovery or removal by solvent extraction using D2EHPA, and cobalt recovery by solvent extraction using Cyanex 272 followed by electrowinning.

Recently, processing of African Heterogenite at Rubamin Ltd, India has been reported by Das (2006). A similar reductive acid leaching with SO_2 as reductant is used under controlled pH. The leach liquor containing Mn, Zn, Cu, Ni, and Fe along with Co is first neutralised with lime to precipitate most of the Fe and Cu, followed by extraction of Mn and Zn from the leach liquor by D2EHPA, and then extraction of cobalt by phosphonic acid (P507, produced in China). Nickel in the raffinate is recovered as nickel carbonate. The electrolytic cobalt produced at Rubamin has a purity of 99.9%. The overall recovery of cobalt from heterogenite is more than 90% together with production of a wide range of salts of cobalt, copper, nickel, and manganese.

4.3. Treatment of waste batteries

Lindermann et al. (1994) described the Batenus process for recycling battery waste. The crushed batteries were leached in sulfuric acid. Several techniques were employed for the separation of metals.

1. The insoluble manganese dioxide and carbon residue were sold to the ferro-manganese industry and the metal salt solution was treated by ion exchange to recover copper, nickel, cadmium, and mercury. The zinc was recovered by solvent extraction.
2. The manganese from the leach solution was precipitated as carbonate from the raffinate.
3. The remaining alkaline metal sulfate and chloride solution were separated into acid and base by electro-dialysis with bipolar membranes.

The Batenus process was reported to be free of any emission, and produce raw materials with remarkably high purity. The zinc, nickel, cadmium, copper, and mercury were separated out of the used zinc-carbon, alkaline manganese, and nickel-cadmium batteries. Moreover, the manganese carbonate, obtained as raw material, could be used for the production of manganese dioxide for new batteries.

A hydrometallurgical process for the recovery of zinc and manganese from spent batteries was developed by Bartolozzi et al. (1994). In this process, the spent batteries was leached with 32% sulfuric acid, and after liquid and solid separation, the dissolved iron was removed by precipitation by NaOH at pH 3.7 and then by 32% ammonia at pH 5 and 60 °C with addition of small amount of H_2O_2. The subsequent solution was first electrolysed to remove Hg, Ni, and Cd, and then at pH 3.7 was electrolysed to recover cathodic zinc and anodic MnO_2. The Mn(IV) in the leach residue was solubilised in acidic hydrogen peroxide (35%) and re-precipitated with NaOH at 40 °C. This process appears feasible technically, but hardly likely to be applied economically with so strong conditions and the use of expensive reagents such as H_2O_2 and NaOH to recover manganese dioxide.

For treatment of waste lithium battery, Shibata and Baba (1995) investigated a process in which lithium and manganese were selectively leached from the battery by using diluted mineral acids HCl and HNO_3. Lithium and manganese were precipitated as their carbonates from the individual leached solution with sodium carbonate solution.

A process for recovery of metal values from chemical by-products of spent Mn–Zn batteries was reported by Ptitsyn et al. (2001b). The by-products from spent Mn–Zn batteries were processed by grinding, magnetic separation of iron scraps, firing the powders, acidic leaching, and electrowinning of zinc on the cathode and MnO_2 on the anode.

4.4. Treatment of Mn-bearing sludges and slags

Kukula and Sikora (1977) reported a hydrometallurgical process for the recovery of manganese from slag leaching solutions. The solution contained (g/L) SiO_2 15–20, Mn 25 and $(NH_4)_2SO_4$ 197, and (mg/L) Cr 1.5, Ni 2.76, Co 7.78, Cu 5.4, Mo 0.95 and Fe 800. The purification was accomplished by the following procedure:

1. SiO_2 was removed by precipitation with lime.
2. Fe^{2+} was precipitated as $Fe(OH)_3$ after oxidation with $KMnO_4$.
3. Nickel and cobalt were removed partly by co-precipitation with iron, partly by reduction with manganese dust added.
4. The excess of cobalt was extracted by solvent extraction, and the organic impurities were removed by adsorption on active carbon.
5. From the pure solution, manganese was recovered electrolytically on aluminium cathode at current density 300–400 A/m^2 in a membrane system.

The feasibility of this process would depend on the initial concentrations of manganese and other valuable metals such as cobalt and nickel in the solution. For this particular case, the initial cobalt content is considered too low to be feasible.

A process for the recovery of manganese from electrolytic zinc anodic slime and from scrap dry cells described by Yoon and Kim (1986) involved the following steps: (a) manganese was extracted from anodic slimes of electrolytic zinc anodic slime and scrap dry cells by leaching with HCl. (b) The impurities (Zn, Fe, Pb) were removed from the leach solution prior to electrolysis by neutralization with NH_4OH and cementation with manganese powder. (c) The manganese was electrodeposited from the purified chloride solution with added Na_2SeO_4. However, evolution of Cl_2 during leaching and electrowinning are likely to be issues and consumption of ammonia is expected to be high.

A process for recovery of Zn and Mn from a water treatment plant sludge was developed (Pesic et al., 1996; Binsfield et al., 1996). The process features leaching of the sludge with H_2SO_4 in the presence of SO_2 reductant at pH 2 and 60 °C for 15 min, three-stage purification, and simultaneous electrowinning of zinc and MnO_2.

6. Conclusions

The major and potential manganese sources, routes and products are graphically summarised in Fig. 5.

Rich manganese ores (>40% Mn) are dominantly processed by pyrometallurgical processes to produce ferro-Mn and silico-Mn alloys, which are mainly used in iron and steel industry. Production of CMD, EM and EMD are mainly accomplished by reductive roasting followed by hydrometallurgical processing. Low manganese ores (<40% Mn) and polymetallic manganese nodules currently cannot be economically processed by pyro-processes because too much energy is required.

A number of hydrometallurgical processes have been developed, both in acidic and basic media. Among the various methods developed, the reductive leaching of Mn(IV) to Mn(II) has been extensively investigated, including the reductants of aqueous SO_2, ferrous salts, reducing organics, H_2O_2, sulfide minerals, bio- and electro-reduction. Among these processes, the sulfur dioxide reductive leaching process has been developed to a pilot scale for processing of manganese ores and manganese nodules. One problem to use SO_2 as the reductant is the formation of dithionate by-product. It can be minimised by controlled the addition of SO_2 to achieve a desired solution Eh as developed by HiTech Energy Ltd.

However, the crucial issue is the purification of leaching liquors due to the extraction of iron and manganese in the course of leaching operations. Selective recovery of Cu, Ni and Co is often difficult from solutions containing soluble iron and manganese as contaminants. The leaching processes of ocean manganese nodules can be conducted in near ambient conditions, using cheap and readily available chemicals. Selective recovery of Cu, Zn, Ni and Co components is possible over manganese with ammoniacal sulfite alkaline leach. In this strategy, Cu, Zn, Ni and Co metals are extracted into solution as ammines whilst iron and manganese is stabilised in residue as hydroxide, oxides and carbonate.

The main methods for recovering manganese from the leach solution include electrolysis for EMD production, electrowinning for EM production and chemical process for CMD production. Purification steps are needed, depending on what product is produced. Generally, iron and aluminium impurities are removed by hydroxide
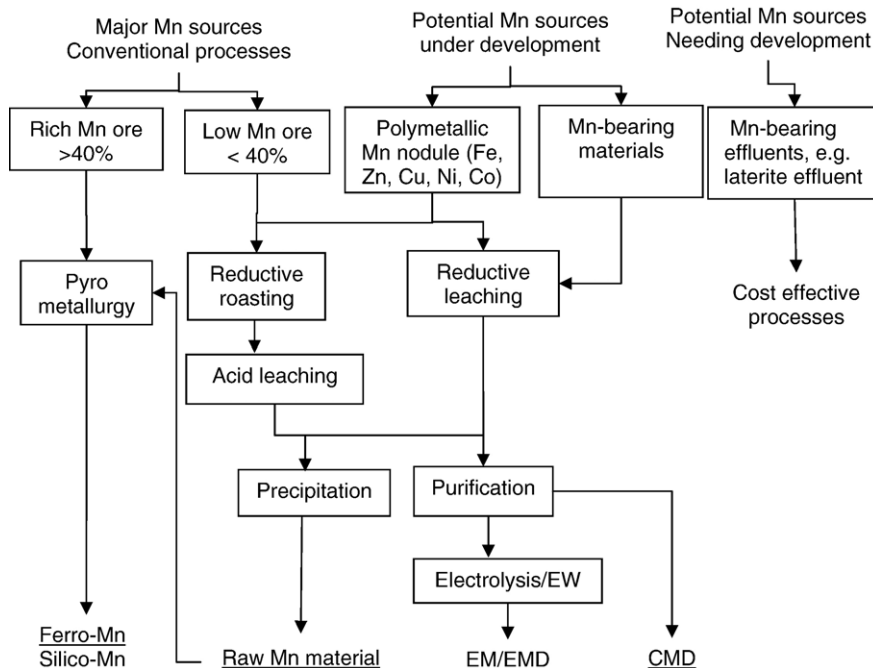

Fig. 5. A schematic diagram of major and potential manganese sources, process routes and products.

precipitation and other base metals removed by sulfide precipitation. Jarosite precipitation is required for removal of potassium ions for the production of EMD. In recent development by HiTech, solvent extraction has been used to recover manganese from the leach solution and enable early rejection of the majority of impurities.

One of the potential sources of manganese, which has not received much attention, is the recovery of manganese from industrial waste solutions, particularly from Ni-Co laterite high pressure acid leach effluents which contains about 1–5 g/L Mn together with other impurities. This is the focus of Part II of this review which considers the application of various solvent extraction reagents and precipitation methods.