Production of Silicomanganese Alloy from Low Manganese Containing Leached Sea Nodules Residue

R. K. Jana and N. S. Randhawa
National Metallurgical Laboratory, Jamshedpur, India

ABSTRACT

Leached sea nodules residue was used for the present study for exploring its utilization. The residue generated in ammoniacal-SO_2 pressure leaching was water washed to reduce the sulphur content. To improve the Mn/Fe ratio in the residue, it was blended with Fe-Mn slag or Mn ore in the calculated amount and smelting was carried out in 50 kVA submerged arc furnace. Various parameters such as holding time, amount of reductant, power input etc. were investigated. The maximum recovery of Mn from residue blended with Fe-Mn slag and Mn ore was 58% and 65% respectively in the form of silicomanganese.
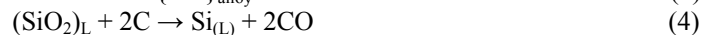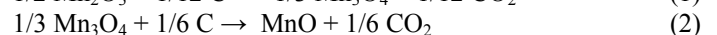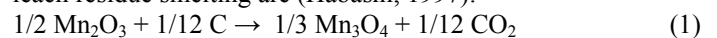
KEY WORDS: Sea nodules; Sea nodule leach residue; Characterisation; Blending with Mn containing materials; Smelting; Silicomanganese; Submerged arc furnace

INTRODUCTION

The most extensive deposit of manganese oxides are found in the world's oceans, which is known as polymetallic sea nodules or deep-sea manganese nodules or ferromanganese nodules that are 0.5–25 cm in diameter, with an average diameter of ~4 cm. Polymetallic sea nodules are also important resource of strategic metals like copper, nickel and cobalt. Several processes have been developed in various parts of the world to recover these metals (Xueyi et al, 1997; Agarwal and Goodrich, 2003), although none of them is in the stage of commercially exploitable, may be due to some mining and environmental hurdles (Manickam et al , 1996). In India, a pilot plant for the treatment of polymetallic nodules to recover copper, nickel and cobalt was set up at Hindustan Zinc Limited, Udaipur by Ministry of Earth Sciences, Govt. of India (Mittal and Sen, 2003). This is based on the Ammoniacal pressure leaching in presence of sulphur dioxide (Das et al, 1998; Das et al, 1999; Das, 2001). This process generates huge amount of residue (70-75% of treated nodules) after leaching of Cu, Ni & Co from the nodules. The leached residue mainly contains manganese, iron and silicon along with some quantity of lime, magnesia, alumina etc. The leached residue may be subjected to smelting along with reductant and flux in a submerged arc furnace to produce ferrosilicomanagnese alloy (Tolsoguzov et al 1995; Rusakov et al, 2004), which is widely used during steel making. This will also improve the economics of the polymetallic sea nodules processing.

Although the Mn/Fe ratio (2.5) in leached residue is not favorable to process it directly to produce standard grade ferrosilicomanganese alloy (Narayanan and Subramanyam, 1959), it can be blended with a high manganese containing material to get the desired Mn/Fe ratio. Residue also contains considerable amount of sulphur due to leaching of the of sea nodules in ammoniacal-SO_2 medium. The metal sulphates decompose at higher temperature during smelting leading to evolution of SO_2 gas. In the reducing atmosphere of reduction smelting, SO_2 reduces and sulphur is transferred to the slag which is eventually transferred to the alloy phase (Turkdogan, 1983). High sulphur in ferrosilicomanganese may be detrimental for using it in steel making process. Therefore, sulphur needs to be removed from leached residue prior to smelting. In the silicomanganese smelting, the overall efficiency of the process depends upon the MnO reduction in the melt whether the raw material is high grade ore or low grade material such as leach residue. In leach residue, manganese is mainly in the form of Mn_2O_3. The reduction of Mn_2O_3 is much easier than MnO as MnO requires higher reduction potential (Habashi, 1997). The kinetics of the MnO reduction by carbon and the effects of different parameters have been studied by several investigators (Yastreboff et al, 2003; Shimpoo et al, 1984; Daines and Pehlke, 1971). The basic reactions pertaining to silicomanganese from leach residue smelting are (Habashi, 1997):

$$1/2\ Mn_2O_3 + 1/12\ C \rightarrow\ 1/3\ Mn_3O_4 + 1/12\ CO_2 \qquad (1)$$
$$1/3\ Mn_3O_4 + 1/6\ C \rightarrow\ MnO + 1/6\ CO_2 \qquad (2)$$
$$MnO + C \rightarrow \{Mn\}_{alloy} + CO \qquad (3)$$
$$(SiO_2)_L + 2C \rightarrow Si_{(L)} + 2CO \qquad (4)$$

Theoretically, reaction in Eq. 3 is rendered feasible at temperature 1400-1500°C and that in Eq. 4 is feasible above 1550°C. Hence, the temperature plays a critical role in determining the final composition of the alloy phase. The purpose of the present study was to determine the amenability of leached sea nodules residue for the production of standard grade ferrosilicomanganese alloy by high temperature carbothermic reduction in a submerged electric arc furnace.

EXPERIMENTAL

Materials

The leached sea nodule residue (SNR) was received from the sea nodules pilot plant at Hindustan Zinc Limited, Udaipur, India. This was subjected to water washing with SNR to water ratio of 1:10 in an agitator. The slurry was filtered using 'Sparkler' plate & frame type filter press. The washed sea nodules residue (WSNR) was dried at 110°C for 5 hrs. and analysed for sulphur and other components. Thereafter, it was pelletized to make 5-15 mm size pellets on disc pelletiser using binder (Bentonite, 2% by mass) and water.

Manganese Ore India Limited, Nagpur supplied the manganese ore whereas ferro-manganese slag material was procured from M/s Khandelwal Industries, Nagpur, India. The coke used in these studies was of high grade with low ash content. The flux materials viz. quartz and limestone were of commercial grade.

All the raw materials except sea nodule residue were crushed and 5-15 mm size fraction was taken for charge mix (CM) preparation.

Characterisation of SNR & WSNR

Dried sea nodule residue (SNR) and washed & dried sea nodule residue (WSNR) samples were analysed for chemical composition by standard wet methods for major elements and by Atomic Absorption Spectrometer for minor elements. The residue was also analyzed for the mineralogical phases by a Siemens D 500 X-ray diffractometer using $FeK\alpha/CoK\alpha$ radiations. Particle size of SNR was determined using Malvern SA-CP3 particle size analyzer. TG-DTA analysis of WSNR was carried out in SEIKO, SSC/5200 analyzer at heating rate of 10°C/min in normal condition.

Smelting in 50 KVA submerged electric arc furnace

The smelting of charge material was carried out in 50 KVA submerged electric arc furnace. The furnace consists of a rectangular mild steel shell having magnesia-carbon brick lining with a top lined with castable material Whytheat A. It is equipped with two graphite electrodes having water-cooling system for electrode holders. A schematic diagram of the furnace is given in Fig 1.

In a typical smelting trial, the furnace interior was preheated with fuel gas for 3 hours before arcing. The arcing was struck by placing 100 gms. coke and lowering the electrodes. As the arc started between the electrodes, the charge material was added at the appropriate rate and after complete melting, extra time (i.e. holding time) was provided for the completion of the reactions and proper separation of metal and slag phase. The average power input during the smooth operation was maintained at 700 Amps and 40 Volts. After the smelting, the molten mass was tapped in a preheated graphite crucible by opening the tap hole and a IR Pyrometer Ircon 'Ultimax' was used to measure the taping temperature.
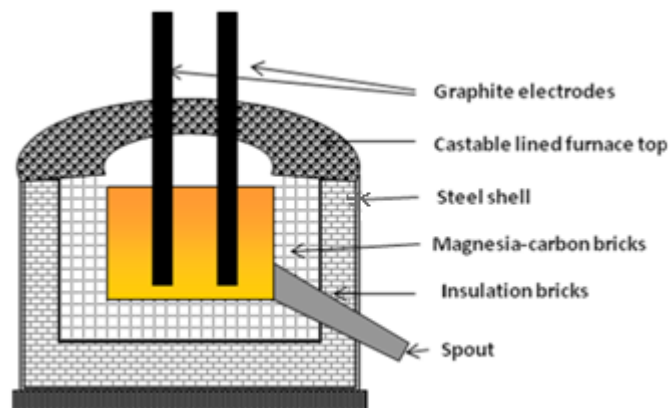

Fig. 1 Schematic diagram of electric arc furnace

RESULTS & DISCUSSIONS

Characterisation of raw materials

The chemical composition of leached sea nodule residue (SNR) and washed residue (WSNR) is given in Table - 1. The major elements are found to be Mn, Fe, Si. It may be noticed that metal content in the washed residue increased to some extent mainly due to removal of soluble metal sulphates and ammonia. However, the increase in manganese content in washed residue was found to be less compared to iron and silicon. This is perhaps due to more solubility of manganese sulphate which was absorbed in the leach residue. The composition of other raw materials such as ferro-manganese slag, Mn ore, limestone, quartz and coke are given in Table - 2.

Table 1. Chemical composition of sea nodule residue (SNR) and washed residue (WSNR) in wt. %

Element/Oxide	Unwashed residue	Washed residue
Mn	22.20	25.46
Fe	8.98	12.41
Si	7.53	10.08
S	3.38	0.16
P	0.15	0.15
NH_4^+	1.60	Not found

The particle size analysis of the leach sea nodule residue is given in Fig. 2, which depicts the very fine nature of the residue. The top size of the particles in the sample is 90-micron. However, about 50% of the material has size below 20 micron and sizable amount (~17%) of the particles has 5-10 micron size.

Table 2. Chemical composition of blending material, reductant and fluxes (in wt. %)

Material		%, by mass
Ferro-manganese slag	MnO	35.5
	FeO	0.80
Manganese ore	MnO_2	78.54
	Fe_2O_3	9.9
Reductant	Fixed carbon (%)	85.5
	V.M. (%)	1.5
	Ash (%)	10.25
Quartz	SiO_2	98.0
Limestone	CaO	49.0

The XRD of air-dried SNR and WSNR are given in Fig. 3. The samples are mostly amorphous in nature with lack of crystallinity. Due to this, a few low-intensity peaks corresponding mainly to Mn_2O_3 and SiO_2 were identified. TG-DTA analysis of SNR and WSNR are presented in Fig. 4. The unwashed leached residue (A) shows multiple endothermic peaks. The first-stage weight loss (~12%) with an endothermic peak corresponds to the loosely bound water molecules. The second

Fig. 2 Particle size distribution of sea nodule residue.
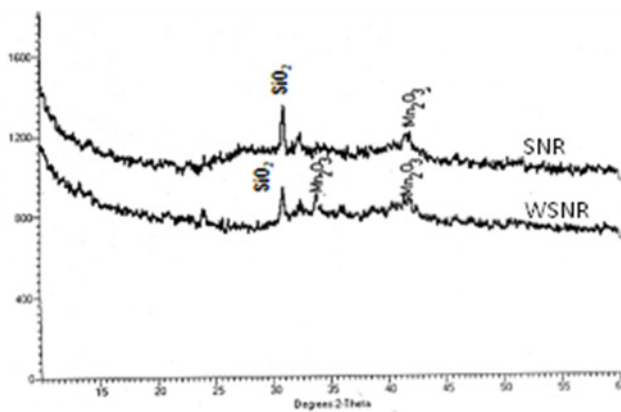
Fig. 3 XRD diffraction pattern of SNR & WSNR

stage loss (~18%), along with two endothermic peaks, is mainly attributable to the decomposition of ammonium sulfate as well as structural water from hydrous oxide and clay minerals. The weight loss above 700°C, with two broad endothermic peaks at ~800 and 1050°C, is presumably due to the decomposition of oxide phases and small amount of metal sulfates formed in the process of leaching respectively. In contrast, the water-washed sample (B) shows a continuous weight loss with two endothermic peaks at ~80 and 420°C, which are mainly attributable to physisorbed and structural water respectively. About 9% lesser weight loss observed with the water-washed sample as compared to the unwashed leached residue is perhaps, due to removal of sulfate during washing.
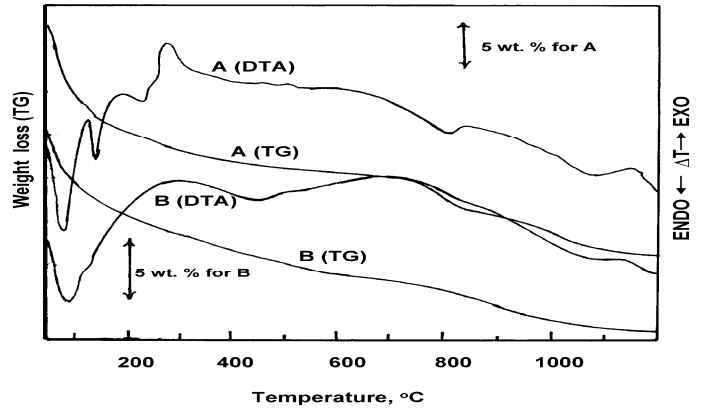

Fig. 4 TG-DTA analysis of (A) SNR & (B) WSNR

Removal of sulphur

The results obtained by washing of leached residue are shown in Fig. 5, which depicts that that nearly 95% sulphur has been removed in 1.5 hrs. by washing with water. This indicates that most of the sulphur in the leached residue is in water soluble sulphate form.
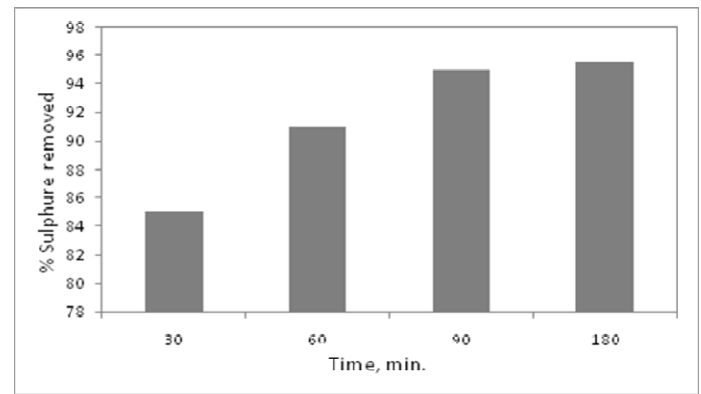

Fig. 5 Removal of sulphur at solid: liquid ratio of 1:10

The washing has also slightly improved the manganese content of the residue as evident from the chemical composition given in Table - 1. In all the smelting experiments WSNR pellets were used for charge preparation.
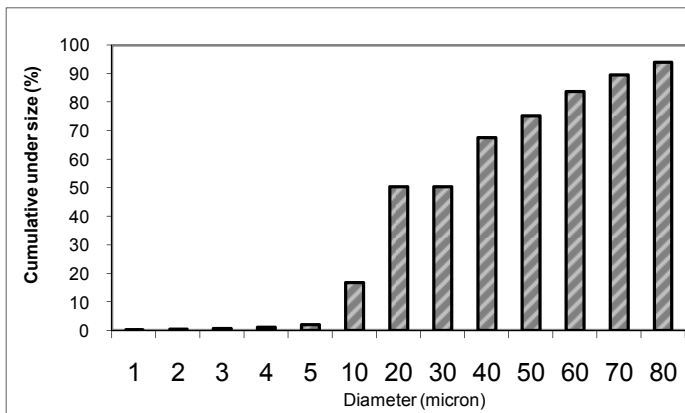
Improvement of Mn/Fe ratio in the washed residue

The sea nodule does not have the favourable Mn/Fe ratio for the production of standard grade Fe-Si-Mn (2:1 against the desired ratio of 3:1 or more).
To improve this ratio, two options were tried:-
1. Calcination of leached residue with coke followed by magnetic separation to remove iron.
2. Blending the residue with low iron containing manganese ore or slag e.g. Fe-Mn slag.

Calcination of washed residue followed by magnetic separation

The washed sea nodule residue was mixed with 5% coke powder (w/w) and pelletized using required amount of water, then dried and calcined in pot furnace at different temperature and time. After calcinations, 100 gms pellets were cooled, crushed and ground to pass through 200# sieve and subjected to wet magnetic separation using low intensity drum magnetic separator. The magnetic and non-magnetic fraction of each experiment and the corresponding chemical analysis is given in Table 3., which shows that the magnetic fraction has increased from Exp. 1 to 4.

Table 3. Composition of magnetic and nonmagnetic fraction

Sam. ID.	Condition	Chemical composition			
		Non-Magnetic			
		Grams	%Fe	%Mn	Mn/Fe
CWSNR – 1	650°C/ 1.0 hr	91.68	12.16	26.17	2.15
CWSNR – 2	650°C/ 1.5 hr	82.73	12.19	26.29	2.16
CWSNR – 3	750°C/ 1.0 hr	79.35	11.87	26.02	2.19
CWSNR – 4	750°C/ 1.5 hr	66.95	11.62	25.97	2.23
		Magnetic			
CWSNR – 1	650°C/ 1.0 hr	8.32	15.14	23.71	1.57
CWSNR – 2	650°C/ 1.5 hr	17.27	15.25	24.23	1.59
CWSNR – 3	750°C/ 1.0 hr	20.65	14.86	25.64	1.72
CWSNR – 4	750°C/ 1.5 hr	33.65	13.96	25.84	1.85

The chemical composition of nonmagnetic and magnetic fraction show that the Mn/Fe ratio in the nonmagnetic fraction is more than that of magnetic fraction but still much lower than the minimum required value. On the other hand, a significant quantity of manganese also goes with magnetic iron oxide in the magnetic fraction. Therefore, both of these fractions could not be used for charge preparation owing to their low Mn/Fe ratio.

Blending of washed residue with ferromanganese slag and Mn ore

Two different manganese containing materials viz. Fe-Mn slag and manganese ore were used for blending. Therefore, two charge compositions were formulated (i) WSNR pellets mixed with Fe-Mn slag and (ii) WSNR pellets mixed with Mn ore. They were mixed with required quantity of coke and fluxes and designated as CM-1 and CM-2 respectively. The charge composition, blending ratio and resulting grade of manganese and Mn/Fe ratio are given in Table - 4.

Table 4. Composition of charge mix

	CM – 1	CM - 2
WSNR (gm)	10000	10000
Fe-Mn slag (gm)	10000	-
WSNR: Fe-Mn slag	1:1	-
Mn ore (gm)	-	7000
WSNR: Mn ore	-	1:0.7
% Mn in blended material	26.6	35.3
Mn/Fe ratio	4:1	3.5:1
Coke (gm)	4000	4000
Quartz (gm)	850	2500
Limestone (gm)	850	1000

Smelting of blended charge in submerged arc furnace

The charge composed of washed residue pellets, blending material (Fe-Mn slag or Mn ore), coke and flux (Table 4)were smelted in submerged electric arc furnace. The temperature of the melt was kept around 1650°C as the reduction of manganese and silicon dioxides were feasible only around 1400-1500°C and 1600°C respectively (Riss and Khodorvosky, 1967). The various parameters in the smelting of blended charge such as holding time, power input etc. were studied. The coke was added in excess of the stoichiometric requirement to maintain reducing atmosphere. The target composition of silicomanganese was Mn: 63-65%, Si: 14-18%, C: <2.5%, S: <0.03% and P: <0.30%. (Bureau of Indian Standard, 1990). Fluxes were added to control the basicity (CaO+MgO/SiO$_2$) of slag in such a way that the distribution of Mn and Si would result in required composition of silicomanganese alloy (Rankin, 1979). The effect of addition of CaO (as limestone) can be explained in terms of the breakup of silica network with the addition of basic oxides. The strong interaction between Ca^{2+}, Mg^{2+} and silicate ions (Kubaschewsky et al, 1979; Pankratz et al, 1978) result in free Mn^{2+} ions which kinetically associate with free oxygen in the slag and increases MnO activity in the slag. The high MnO in the slag favours the transfer of Mn into metal (Stukel and Cocubinsky, 1954; Turkdogan and Hancock, 1958). Moreover, the final silicomanganese alloy should contain 14-18% of Si metal. The simpler method to increase the Si in the metal is the addition of silicious material (quartz) and maintaining high temperature required for reduction of silica to silicon.

Chemical composition of alloy

The Mn & Fe content of alloy produced was found to conforming with the standard grade alloy for both the smelting trials. The alloy compositions and corresponding slag compositions are given in Table – 5 and Table – 6 respectively. The sulphur and phosphochrous content of the silicomanganese alloy produced was well within the stipulated limit for a standard grade alloy (Bureau of Indian Standard, 1990). The Si content largely depended upon the amount of reductant. Fig. 6 shows the variation of Si content in alloy as function of carbon addition in charge. There was an increase in the silion content of metal with increasing carbon addition for smelting of both the CM-1 and CM-2 charges at slag basicity of 0.8.

Table 5. Chemical composition of ferrosilicomanganese alloy obtained by smelting of CM-1 and CM-2 (recovery of individual metal given in parentheses)

Charge material	Holding time (min.)	Chemical composition, wt. %					
		Mn	Fe	Si	C	S	P
CM-1	60	63.2 (58.0)	16.4 (65.7)	15.6 (36.3)	2.23	0.009	0.15
CM-2	45	64.4 (65.0)	17.01 (74.2)	15.9 (30.4)	2.14	0.015	0.21

Table 6. Chemical composition of slag obtained after smelting of CM-1 and CM-2

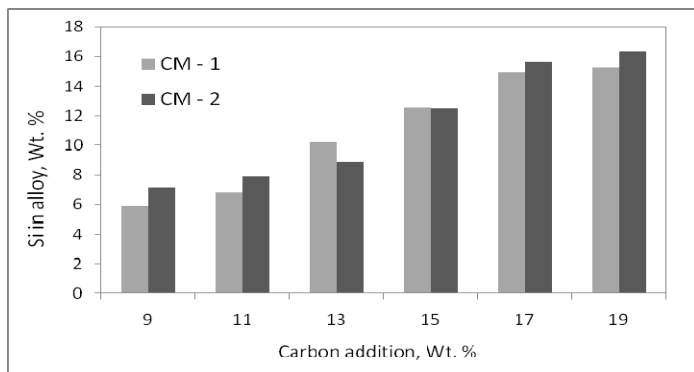| Charge material	Holding time (min.)	Chemical composition, wt. %					
		MnO	FeO	SiO_2	CaO	MgO	Al_2O_3
CM-1	60	17.42	2.51	27.5	18.5	5.14	9.5
CM-2	45	15.37	5.07	35.5	25.6	4.5	2.75

Fig. 6 Variation of Si content in metal as a function of fixed carbon added in the charge

Effect of holding time on manganese recovery

Effect of holding time on the manganese recovery after complete melting of the charge is shown in Figure - 7.
For CM-1, it was found that the recovery of manganese in the alloy increased with the holding time and reached to the highest value (58%) after about 60 minutes of holding time.
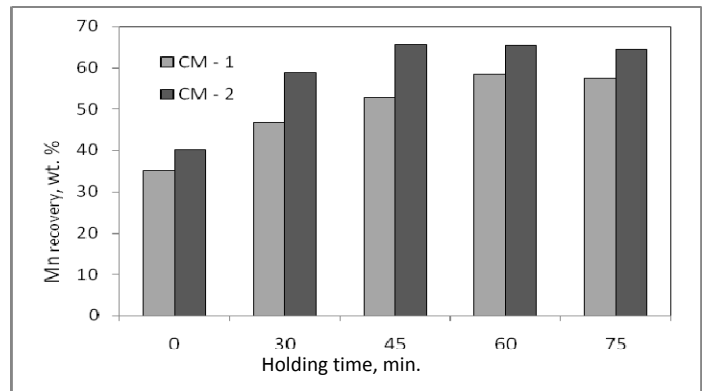
Fig. 7 Effect of holding time on the recovery of manganese

For CM-2, the maximum manganese recovery was achieved at holding time of 45 min. and after that there was no change in the manganese recovery. It may be noted that on blending the charge with manganese ore the recovery of manganese was higher (65%).

Effect of power input on Mn recovery

The power input was optimised with the view that the temperature of the molten mass should be around 1600°C to ensure the satisfactory reduction reactions. Power input was found to be 17.5 and 10 KWH/ kg of alloy for charge type CM-1 and CM-2 respectively for maximum recovery of manganese as depicted in Fig. 8.
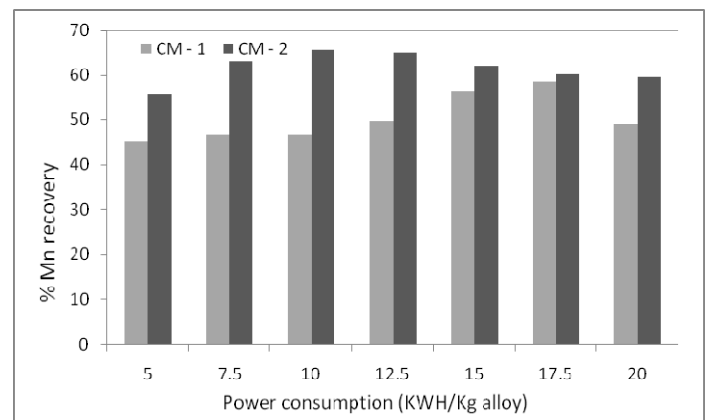
Fig. 8 Effect of power input on Mn recovery in alloy for holding time of 60 minutes

Higher power consumption was noted in the smelting of CM-1. It may be due to the presence of complex Mn and Fe silicates in the blended Fe-Mn slag, which might have consumed higher power. It was also observed that increased power input resulted in better metal-slag separation. The Mn recovery decreased with further increase in power input, due to the vaporization loss from the alloy phase at higher temperature. The lower recovery of Mn (58.5%) in smelting of CM-1 is perhaps, due to the high slag to metal ratio (5:1). In case of CM-2, this ratio was 2. Overall low recovery of metals in both the charges may be due

to the use of low grade materials like leach residue, ferro-manganese slag etc. in the charge (Voronov and Gavrilov, 1996).

CONCLUSION

- Water washing of the leach sea nodule residue, generated from ammonia-SO_2 leaching process, is required for removal of sulphate & ammonia to achieve the acceptable quality of the Fe-Si-Mn.
- Standard grade Fe-Si-Mn can be produced by blending the leach residue with Fe-Mn slag or Mn ore.
- The silicon content of the alloy was found to depend on carbon addition in charge, which increased with increasing amount of carbon addition.
- The Optimum holding time for charge blended with manganese ore and ferromanganese slag was 45 min and 60 min. respectively.
- Better manganese recovery (65%) with lesser power consumption was found when the residue was blended with manganese ore.

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