



EXTRACTION OF SILICOMANGANESE FROM MARINE AND LOW GRADE MINERAL RESOURCES

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ABSTRACT

Manganese nodule, available in ocean beds, is a potential resource of the future for copper, nickel and cobalt. Recovering only these metals, containing less than 3% by weight, will result in the generation of large amount of residue. In addition to the material losses, several environmental and ecological problems arise out of this. The present study has been aimed at reducing the environmental and ecological problems associated with massive generation of this residue together with utilization of the resources. Presence of ~ 20% manganese and ~16% silicon in the residue has prompted us to check its suitability as a raw material for silicomanganese production. Lower manganese content and lower Mn/Fe ratio of the residue than that required for silicomanganese production has been corrected in this study by suitable blending. The efficacy of blending and its thermodynamic aspects using FACTSAGE software are discussed. The studies conducted indicate viability of bulk utilisation of the residue through silicomanganese production and thereby reducing the burden on environment to a great extent.

1. INTRODUCTION

Rapid depletion of meagre nonferrous metal resources have stimulated efficient use of available land based resources and vigorous search for new sources. Manganese nodules available in the beds of Pacific, Atlantic and Indian Oceans appear to be a solution for copper, nickel and cobalt. Concentrations of these metals are comparable to some of the land-based resources. Availability of these metals in the ocean beds (in manganese nodules) is much more than that in the terrestrial resources. Generally these nodules contain a little over 2% of copper, nickel and cobalt together, ~10% iron, 20% manganese and around 18% silica. So far the attempts have been to extract copper, nickel and cobalt from these nodules due to (1) strategic reasons and (2) their fast dwindling deposits. Though manganese is the major element in ocean nodules, little attempt has been made on its extraction owing to its extensive terrestrial deposits. For processes focussed only on copper, nickel and cobalt, which constitutes less than 3% of the nodules, large amount of residue is inevitable. This would be quite undesirable from the material conservation and process economics point of view. Besides, the environmental and ecological problems associated with this residue are also of great concern. Utilization of this residue for value added products would be a better option to address the concerns mentioned above. Use of these residues as catalyst and/or as an adsorbent for some of the heavy toxic elements is notable among them [1, 2] though their consumption in these applications will be meagre compared to their expected generation. High volume utilization of these residues has been tried in the production of manganese alloys [3, 4]. The main problem of the residue (and many other low manganese resources) has been their low, and hence unfavourable, Mn/Fe ratio (2:1) for production of the manganese alloys [3]. This drawback has been overcome suitably and has yielded standard grade silicomanganese [3, 4].

The present paper contains a brief theoretical analysis of silicomanganese production to determine the product composition (viz. metal, slag and gas) and a comparison of the effectiveness of two blending materials viz. high-grade manganese ore and Fe-Mn slag.

There is little information, other than that mentioned earlier, available in the literature on the utilization of the leach residue in silicomanganese production. Generally, silicomanganese is produced in electric arc furnace by carbothermic reduction of manganese oxides and quartz or other silica sources. Out of the large number of reactions taking place during the process, reduction of MnO and SiO₂, given below, are the vital ones [5, 6].



These two oxides are much more stable than other oxides normally encountered in manganese alloys production and hence need higher temperature & lower oxygen potential for their reduction to metallic state. Higher oxides of manganese are reduced to MnO by topochemical reactions [7] at lower temperatures and hence it appears that the nature of the manganese phase would not matter much. For ores containing silicates, lime has been added to increase the activity of MnO [6]. Being less stable, iron oxides get reduced progressively to its metallic state before the reduction of MnO and SiO₂ and as a result, practically all iron reports to the alloy phase. As a result, selective reduction of manganese cannot be attained through manoeuvring of the operating parameters and this restricts the use of resources with low Mn/Fe ratios. Further, the requirements of higher manganese reduction/recoveries are contrasting to that of silicon; a basic slag for manganese and an acidic slag for silicon reduction. Composition of the charge and the operating conditions, hence, need to be balanced to have good recovery and desired grade.

In manganese alloy smelting, activity of manganese (II) oxides has been reported to be critical in getting good recovery of manganese [8]. Reports suggest that secondary raw materials such as slag etc. in the charge may affect the recovery of manganese adversely [9]. Partial replacement of lime by MgO increases the melting temperature as a result of the increased in resistivity [10], which in turn enhances the grade and recovery in silicomanganese alloy production. It is reported that silicon in combination with carbon is a better reductant in manganese alloys smelting than silicon alone [11]. Quartzite-coke [12] has been found to be better, in terms of recovery and grade of manganese, than metallurgical coke. Silicothermic reduction of slag [13] has also been tried for the production of silicomanganese.

In silicomanganese process, the manganese reduction is slower and corresponds to the second stage described by Skjervheim & Olson [14]. The slow reduction rate in silicomanganese process is also attributed to the decreased MnO activity due to the presence of Al₂O₃ and/or SiO₂. Molten iron dissolves manganese and reduces the activity of manganese and this drives the reduction of MnO to maintain the (MnO)/[Mn] ratio required for the prevailing condition. With the increase in silicon content of the alloy, carbides become less stable and silicides becomes dominant [5, 6] which imply the carbon content of the alloy decreases with increase in silicon content.

Low manganese-high iron ores can also be used for making silicomanganese after converting it to a high manganese slag [15]. It is possible to obtain silicomanganese with low sulphur and phosphorous content even from fine substandard manganese bearing materials using plasma technology [16]. The escape of SiO and manganese vapours etc., which are likely in silicomanganese smelting, needs to be minimized suitably to avoid material losses.

2. THEORETICAL CONSIDERATIONS

Thermochemical computations are conducted using FACTSAGE on a typical charge used in our experiments. FactSage is an application software for calculation of phase equilibria in multi-component, multiphase non-ideal systems. It works by Gibbs energy minimization using diverse set of solution models available within

it. A wide range of chemical, environmental, metallurgical, and geological systems can be analyzed with this software.

The moles input to the software is given in Table 1 and corresponds to the charge given at Table 8. Composition of slag and alloy (silicomanganese) has been determined using the software and compared with that of the experimental values. Gas compositions could not be compared, as it is not available.

Table 1: Charge composition in moles used for Factstage analysis

	MnO ₂	MnO	Fe ₂ O ₃	FeO	SiO ₂	CaO	Al ₂ O ₃	H ₂ O	C
Residue	8.332	-	2.23	-	6.73	0.77	0.60	11.57	0
Fe-Mn slag	0	7.5	0	0.167	7.14	4.11	1.53	0	0
Coke	0	0	0	0	0	0	0	0	70.83
Quartzite	0	0	0	0	1.64	0	0	0	0
Total	8.32	7.5	2.23	0.167	15.51	4.88	2.13	11.57	70.83

* Derived from experimental input used in Table No.8.

3. EXPERIMENTAL

Materials & Methods

Sea nodule residue obtained after recovering the copper, nickel and cobalt through SO₂-ammonia leach process is the main raw material. The chemical analysis of a representative leach residue sample used for the present study is given in Table 2.

Table 2: Chemical analysis of sea nodule residue

Element	Wt. %	Element	Wt. %
Mn	18.31	Ca, Mg	1.21
Fe	9.00	Al	1.30
Si	7.54	Moisture	8.33
Cu, Ni Co	0.315	LOI	28.63

Table 3: Chemical analysis of Fe-Mn slag and Mn ore

Element	Wt. %		Element	Wt. %	
	Mn ore	Fe-Mn Slag		Mn ore	Fe-Mn Slag
Mn	41.72	27.5	CaO	0.20	15.36
Fe	10.01	0.622	Al ₂ O ₃	1.92	10.40
SiO ₂	11.40	28.54	MgO	0.23	5.12
P	2.72	0.015	S	-	0.005

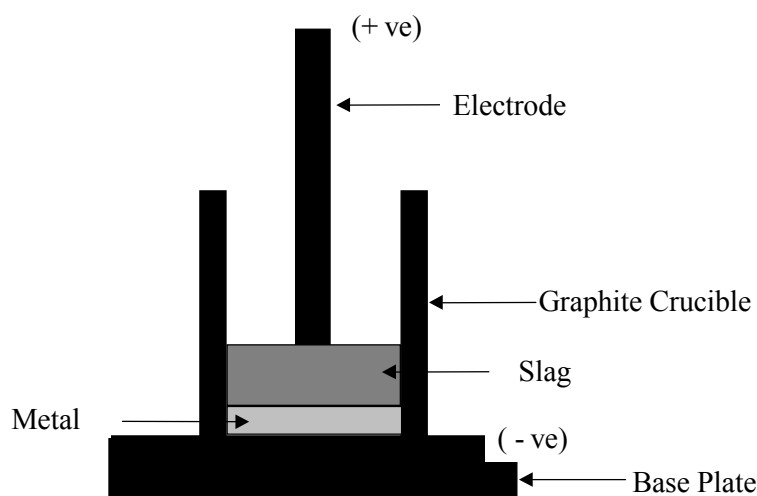


Figure 1: Experimental set up for smelting

Though manganese is the major element in the sea nodule/sea nodule residue, its manganese content is considerably lower than that are being used in ferroalloy industry. Besides, the Mn/Fe ratio of the residue is considerably lower than that required for a standard grade silicomanganese [17]. As the scope of improving the grade of the residue by physical concentration methods is practically nil, the residue has been enriched through blending. A high-grade manganese ore or a ferromanganese slag has been employed for this purpose. Ferromanganese slag used has been obtained from Khandelwal Ferroalloys Corporation, Nagpur, India. The manganese ore has been from indigenous mines. Table 3 gives the chemical analysis of the Fe-Mn slag and manganese ore used in the experiments. Ore contained >40% manganese whereas the slag has the advantage of very low Fe and P content, most of which have been removed during the ferromanganese production. A low ash coke was used as a reducing agent. It had fixed carbon content (FC) of around 85%, and about 12% ash. Various fluxes used in the experiments such as quartzite, foundry sand (98% silica), calcium fluoride, lime etc. were of industrial grade.

Compositions of various raw materials such as leach residue, ferromanganese slag etc. was determined by standard analytical methods. Depending on the concentrations of the elements, wet chemical or atomic absorption spectrophotometer (AAS) was used for analysing. Particle size distribution has been measured using Schimadzu SA-CP3 particle size analyser.

Smelting

The fine nature of the residue, characterised by *D50 of $\sim 10\mu$ and D10 of $\sim 3\mu$ of necessitate its agglomeration to avoid material losses and to have sufficient charge permeability. The sea-nodule residue was pelletised in a drum pelletiser of 0.31 m diameter with 2% bentonite (as binder) to get pellets of 6-8mm size. The green pellets had a crushing strength of 200-250 g and drop strength of about 5 to 7 drops. Pellets were dried suitably in an oven before being charged in to the smelting furnace. (*D_x = y micron means X% of the particle is below y micron)

A single electrode DC arc furnace was used for smelting experiments. The experimental set up, shown in Fig. 1, consists of a graphite electrode, a graphite crucible and a thick graphite plate. The graphite electrode is connected to the positive of the power source. The graphite crucible rests on the graphite plate, which is connected to the negative of the power source. The crucible and the plate together act as the negative electrode

of the system. The graphite electrode, which is connected to the positive of power source, can be positioned at any desired level in the vertical direction with the help of a motorised rack and pinion arrangement. A refractory jacket kept around the crucible prevented the heat losses from the system.

The charge is smelted in the graphite crucible. Small amounts of charge consisting of residue pellets, manganese ore/ferromanganese slag, coke and fluxes, were added to the arc zone in the crucible. As mentioned earlier, manganese ore and ferromanganese ore are used to enrich Mn and hence to correct the low Mn/Fe ratio. As smelting proceeded, further charge addition was made to the crucible. Each of the smelting experiment used about 4-5 kg of charge material. A soaking time of about 40 minutes, after the complete charge addition, at the desired temperature was given to ensure maximum reduction of MnO and SiO₂ and proper slag metal separation. The metal and slag were allowed to cool in the crucible and were separated, weighed and analysed for determining the grade and recovery.

4. RESULTS AND DISCUSSION

Due to the very fine nature of the residue and lack of crystallinity, no sharp peaks were seen in the x-ray diffractogram. However, presence of Mn₂O₃, MnO.Mn₂O₃, Mn₃O₄, Fe₃O₄, FeO and SiO₂ phases are likely in the residue.

5. THERMOCHEMICAL ANALYSIS

Thermo chemical analysis of a laboratory scale experiment, containing leach residue and ferromanganese slag (Table-8) in the charge have been done. The results of thermo chemical analysis using FACTSAGE are given in Tables 4-6. Table 4 contains the composition of the output streams at various temperatures from 1673-1973K for the input given in Table 1. From Table 4 it is observed that the MnO content of the slag decreases with increase in temperature. This is quite expected. As the temperature increases, more MnO gets reduced from the slag phase, most of which report to the alloy phase and the remaining escapes to the atmosphere as vapour. The silica content of the slag, however, shows an increase, reaches a maximum at 1823 K and then declines. On the other hand the (CaO+MnO)/(SiO₂+Al₂O₃) ratio (Table-4) decreases till 1823K and then increases. These two together shows that the manganese reduction predominates till 1823 K and silica reduction accelerates after 1823K.

Fe content (wt.%) of the alloy phase decreased with temperature though it remains same in absolute terms (number of moles). The relative decrease is due to the increase in manganese and silicon entering the alloy phase at higher temperatures. Manganese and silicon in the alloy phase increases with the temperature and can be attributed to the decreased stability of their oxides at higher temperatures. The rate of increase of silicon reduction is less when compared to that of the manganese. Table 5 contains the mole fractions/partial pressures of vapour and gases emanating from the furnace at various temperatures. It is observed that there is increased loss of Mn and Si with temperature. Table 6 depicts the percentage loss of Mn and Si as vapour with increase in temperature. It can be seen that beyond 1873 K, the incremental quantity of manganese reporting to the alloy phase is insignificant. It mainly contributes to the vapour phase only. But to have the required silicon content one has to be above this temperature. Hence a proper balance has to be arrived to have the required silicon content without much loss of manganese. Thermodynamic calculation shows some amount of solid SiC formation at elevated temperatures, which may pose operational difficulties.

Smelting of Leach Residue

Due to the low Mn content and Mn/Fe ratio of the residue, a medium grade silicomanganese alloy viz. Si16Mn63 [17], with Si 14-17% and Mn 60-65% has been aimed. The leach residue was smelted as mentioned above. The results of the experiments using manganese ore as the blending material are shown in Table 7. The grade of the alloy obtained was marginally lower than envisaged as far as manganese and silicon were concerned. However, good recovery of manganese and silicon has been achieved. The low grade of the alloy is due to the high iron content of the charge, most of which is reporting to the alloy under the

Table 4: Composition of FACTSAGE output

	Constituent	Temperature (K)					
		1673	1773	1823	1873	1923	1973
Slag	FeO	Trace	Trace	Trace	Trace	Trace	Trace
	MnO	wt% 37.11 <i>moles</i> 11.71	24.26 5.66	15.32 2.76	8.47 1.14	4.2 0.46	4.1 0.41
	SiO ₂	wt% 41.2 <i>moles</i> 15.37	46.36 12.8	46.6 9.93	40.6 6.47	33.9 4.43	28.2 3.35
	CaO	wt% 12.17 <i>moles</i> 4.87	16.46 4.87	21.33 4.87	28.53 4.87	34.6 4.87	38.2 4.87
	Al ₂ O ₃	wt% 9.8 <i>moles</i> 2.098	12.92 2.098	16.74 2.098	22.39 2.098	27.3 2.098	29.5 2.07
Metal	Fe	wt% 49.32 <i>moles</i> 4.48	27.94 4.48	22.46 4.49	19.69 4.49	19.8 4.49	19.9 4.49
	C	wt% 5.68 <i>moles</i> 2.41	2.61 1.655	1.47 1.375	1.31 1.34	1.4 1.53	1.6 1.68
	Mn	wt% 44.25 <i>moles</i> 4.092	61.06 9.97	62.53 12.73	63.28 14.13	62.8 14.48	62.2 14.31
	Si	wt% 0.17 <i>moles</i> 0.135	8.39 2.69	13.53 5.41	15.57 6.89	16.0 7.27	16.3 7.41
(CaO+MnO)/ (SiO₂+Al₂O₃)		0.97	0.67	0.58	0.59	0.63	0.73

Table 5: Composition (mole fraction) of gas phase using FACTSAGE

	Constituent	Temperature (K)					
		1673	1773	1823	1873	1923	1973
Gas	CO	0.998	0.992	0.987	0.982	0.976	0.968
	Mn	0.0015	0.0063	0.0083	0.012	0.017	0.024
	SiO	-	0.0015	0.0042	0.0066	0.0075	0.0083

Table 6: Loss (@wt.%) of Mn and Si* with temperature in gas phase

	Constituent	Temperature (K)					
		1673	1773	1823	1873	1923	1973
Vapour	Mn	0.2	1.2	2.1	3.4	5.6	8.4
	SiO	-	0.3	1.0	2.0	2.5	2.9

@ with respect to input charge

* as SiO

Table-7: Results of smelting studies (Mn Ore)

Charge Composition (g)		Assay (Wt. %)			Recovery (%)		
S.N.Residue	2500	Mn	Si	Fe	Mn	Si	Fe
Mn-Ore	1000	54.43	14.81	25.45	79	49	99
Silica	300						
Coke	750						
CaO	115						
Alumina	175						
CaF ₂	336						
Power input	17kW						

Table-8: Results of smelting studies (Fe-Mn Slag)

Charge composition (g)		Assay (Wt. %)				Recovery (%)		
		Mn	Si	Fe	C	Mn	Si	Fe
S.N.Residue	2500	61.2	17.9	18.4	1.7	50.7	29.0	56.8
Fe-Mn Slag	1500							
Coke	1000							
Silica	100							
Temperature (°C)	1600-1650							

experimental conditions used in the present study. Increasing the percentage of manganese ore in the charge will help in increasing the Mn/Fe content of the charge, which in turn lead to a grade conforming to standard specification. Since our main aim was to utilise the residue, experiments with increased manganese ore in the charge has not been attempted. An alternative material has been tried instead, to enrich the manganese content and the details are given in the following paragraph. The problem can also be overcome by removing most of the iron from the charge by a first stage smelting wherein most of the MnO are kept unreduced in the slag through proper manoeuvring of the operating parameters. The slag thus obtained will not only be rich but also have high Mn/Fe ratio required in the ferroalloy manufacture, which on further smelting with additional coke ensures silicomanganese of desired grade.

Ferromanganese slag, the alternative enriching material used, contains practically no iron (Table-3) as most of the iron and phosphorous were removed during the ferromanganese production. This has helped in keeping the iron input to the furnace same as that in the residue. The parameters studied included effect of holding time, silica addition etc. The results are given in Table 8. . In general, the slag formed in the experiments with ferromanganese slag addition was viscous and as a result, caused foaming and poor slag metal separation. It is seen that the manganese content of the alloy (~60%) was within the desired level. The silicon content of the metal has also been brought to the desired level with ferromanganese slag blending. However the manganese recovery was around 50% only and this may be attributed to metal entrapment due to increased viscosity of the slag. The low iron recovery substantiates this argument. Low grade and secondary nature of the charge materials like leach residue, ferro-manganese slag etc. may also be responsible for the low recoveries as reported in literature [9]. Low activity of MnO of the charge materials, as reported by Tolstoguzov [8], can also lead to reduced recovery. It can be seen that the results more or less match with grade obtained through thermo chemical simulation using FACTSAGE.

Evaluation of the results, on the basis of the alloy grade obtained, shows that ferromanganese slag is apt for blending the sea nodule residue. The very low iron content of the slag ensured minimum iron input to the charge which helped in maintaining the iron content of the alloy as minimum as possible and thereby pushing the manganese percentage to the higher side. Ferromanganese slag, being a by-product of Fe-Mn production, has little phosphorous content compared to that the manganese ore used. As a result, phosphorous content of the Si-Mn alloy produced was around 0.15% and is well within the stipulated limit (0.3% max.) for a standard alloy [17]. Carbon content of the alloy decreased with increase in silicon content of the alloy as described in the literature [5, 6]. However, the low recovery need to be improved and may be possible by a proper charge optimisation (of residue, slag and ore etc.).

6. CONCLUSIONS

Theoretical studies have shown that manganese and silicon reduction enhanced with temperature though a part is lost as Mn vapour SiO gas respectively. Beyond 1873K, manganese content, in absolute terms, remains same. Beyond this temperature, whatever extra manganese gets reduced is mainly contributes to the vapour phase and hence is lost. The requirements of the silicon and manganese reductions are contrasting and needs proper tuning to have efficient operation. Though good recoveries have been obtained with manganese ore, higher iron content of the charge diluted the product grade (in terms of Si and Mn). Increasing the manganese content alone is not sufficient to obtain a standard grade (Si19Mn63 grade) silicomanganese. It is imperative to have a charge with a high Mn/Fe ratio as well as high manganese content. With ferromanganese slag, alloy with desired grade could be achieved and matches more or less with that obtained by thermo chemical analysis. When Fe-Mn slag was used, the recovery of Mn and Si was low. This is mainly due to metal entrapment in slag & high slag - metal ratio. Blending the sea nodule residue with a suitable combination of Fe-Mn slag and manganese ore will help in improving the recovery of metals. Alternatively, a two stage smelting of residue may be adopted which correct the Mn/Fe ratio without blending. The same process may be extended to other land based ore fines available in plenty but remains unutilised due to their low grade.

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