Thermodynamics and Viscosity Aspects in Manganese Nodule Residue Smelting for Silicomanganese Production

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Abstract Among several under trial processes for extraction of base metals (Cu, Co and Ni) from manganese nodules (MN), the reduction-roast ammoniacal leaching $\{NH_4OH/(NH_4)_2CO_3\}$ process is considered very attractive. After the leaching of base metals from roast-reduced MN, a substantial quantity of residue left behind (about 70 wt. %, by mass) as wastes for disposal or further use. Smelting studies showed that leached manganese nodules residue (WMNR) can be successfully utilized as raw material for silicomanganese production after maintaining proper metallurgical aspects like thermodynamics, viscosity etc. Literature survey on slag liquidus and viscosity aspects of silicomanganese smelting has been done. The slag liquidus has been found to be closely associated to slag basicity i.e. $(CaO+MgO/SiO_2)$ showing significant increase above 0.7 slag basicity. Charge mix basicity of 0.2 was found to give maximum Mn and Si recoveries. Increasing or decreasing charge basicty from 0.2 resulted in lower metallic yield and Mn and Si recoveries. This has been explained with liquidus calculations of final slags obtained at those charge mix basicities. Addition of CaF_2 during holding time i.e. time given after complete melting of charge mix was found to be beneficial. The optimum amount of CaF_2 was 4% of WMNR+Mn ore blend, which gave rise to maximum Mn and Si recoveries and metallic yield. Further addition of CaF_2 (>4%) produced a high basicity slag (basicity =0.83) having very high liquidus leading to decrease in metallic yield and Mn and Si recoveries.

Keywords Leached Manganese Nodules Residue, Basicity, Smelting, Silicomanganese, Slag Liquidus, Viscosity

1. Introduction

Wastes from mining and metallurgical industries are notorious for their hazardous impact on living beings. Hence, issues like processing of mining and metallurgical byproducts/wastes such as fines, lean grade ores, slags, dusts, sludges etc., their safe disposal and recovery of metallic values are considered critical from environmental, economic and social point of view[1]. The present work deal with the manganese nodules processing waste, generated after selective recovery of copper, nickel and cobalt by ammoniacal leaching of manganese nodules[2]. The leached residue of manganese nodules is a fine powdery oxide material. Several studies have been carried out to develop the technologies for complete utilization of waste manganese containing materials like high phosphorous manganese slag, high-carbon ferromanganese-byproduct metal etc[3-5]. However, use of such complicated materials require detailed thermodynamic analysis and their effect on partitioning of the main elements viz. Mn, Si etc., between the silicomanganese and slag in the industrial furnaces. The

thermodynamic equilibrium conditions between alloy and slag determine the yield and grade of alloy in silicomanganese smelting.

The MnO, SiO_2, CaO, MgO and Al_2O_3 are the prevailing oxides taking part in silicomanganese smelting reactions in slag. The MnO and SiO_2 undergo reduction by 'carbon' either as graphite or in SiC[6], which can be represented by Eqn (1) and Eqn. (2).

$$(MnO) + `C' = \underline{Mn} + CO_{(g)} \quad (1)$$
$$(SiO_2) + 2`C' = \underline{Si} + 2CO_{(g)} \quad (2)$$
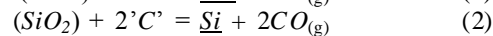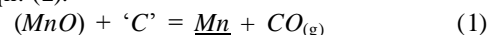
The oxides of CaO, MgO and Al_2O_3 remain entirely in the slag as they are thermodynamically stable in the operating conditions. Presence of these oxides in slag significantly affect the activity of the manganese oxide (a_{MnO}) and silicon oxides (a_{SiO2})[7-9] and hence, the extent of reaction 1 and 2. This determines the distribution of Mn and Si between alloy and slag phase and hence the composition of alloy. Therefore, slag composition needs to be amply maintained to allow favorable distribution of Mn and Si across slag metal interface to recover metals in desired ratio. Slag composition is typically expressed by mass ratio different oxides in the slag[5,6,10], as given in Eqn. (3) and Eqn (4).

$$B(Basicity) = \frac{(CaO+MgO)}{(SiO_2)} \quad (3)$$
$$R \ ratio = \frac{(CaO+MgO)}{(Al_2O_3)} \quad (4)$$

Silicomanganese smelting is generally done with excess silica i.e. acidic slag. Addition of alumina to acidic slag is also found to decrease the equilibrium MnO content in the slag[7]. Several studies have reported that increase in basicity increases the a_{MnO} and decreases the a_{SiO2}, resulting in decreased equilibrium MnO and increased SiO_2[5,7-10]. The viscosity of slag significantly affect the partitioning of metals between alloy and slag phase[11]. A sufficiently fluid slag should always be maintained to avoid metal entrapment in slag so that proper slag-alloy separation can be achieved.

In present paper, some of the thermodynamic and viscosity aspects of leached manganese nodules residue smelting for silicomanganese production are described. Particularly, the dependence of charge mix preparation and Mn distribution on these two aspects are discussed in details.

2. Thermodynamics and Viscosity Aspects in Silicomanganese Smelting

As mentioned above, that reduction of MnO and SiO_2 mainly takes place from slag; and therefore maintaining a sufficiently liquid slag with minimum viscosity at operating temperature i.e. at 1600 ±50℃ is a prerequisite for charge mix preparation. Additionally, the raw materials must be blended in such proportion that would produce slag with minimum MnO content and allow desired distribution of Mn and Si between alloy and slag phase. In silicomanganese production, smelting is carried out in acidic slag i.e. slag basicity<1. Several studies have been done to study the effect of slag basicity on Mn and Si distribution or Distribution Ratio i.e.[ratio of Wt. % metal in slag to that in alloy]. Equilibrium studies on distribution of Mn between Mn-Si-Fe-C alloys and MnO-CaO-MgO-SiO_2-Al_2O_3 slag at 1500℃ under CO atmosphere revealed that an increase in basicity ratio of slag decreases the Mn distribution ratio[12]. In contrast, increase in silica concentration of the slag increases the Mn distribution ratio. The optimum slag basicity B, reported by Chaichenko et al[13] is in the range of 0.65-0.90. Addition of alumina to slag favours transfer of Mn to alloy leading to a low MnO slag. In the studies by Cengizler et al[14] activity data for Fe-Mn slags were modelled by applying neural nets at 1500℃ for slag compositions lying in the range of MnO 5–40%, CaO 4–35%, MgO 0.3–38%, SiO_2 25–60% and Al_2O_3 2.5–7%. Their study concluded that activity coefficient of MnO in liquid slag region varies on both sides of unity. Studies by Tang and Olsen[15] and Ding and Olsen[16] also reported that addition of alumina to acidic slag decreases the equilibrium MnO content in the slag. In acid slags the $\Upsilon_{MnO} < 1$, whereas in basic slags the $\Upsilon_{MnO} > 1$, where Υ is activity coefficient. The basicity of slag keeps on increasing up to the equilibrium value due to reduction of SiO_2 to Si. On the other hand, R ratio practically remains constant throughout the smelting and should be more influencing to slag-metal equilibrium. Nikolaev[10] reported the optimum R value to be 2.5 whereas Emlin et al[17] concluded optimum R value in the

range of 1.2-2.2. Eissa et al[5] studied the smelting of high Mn slag and observed the highest metallic yield and recoveries of manganese and silicon with initial R value of 1.8 by using dolomite as fluxing material. They also concluded that slag basicity adjusted by addition of dolomite gave higher metallic yield, manganese and silicon recoveries comparing with that obtained by adding either limestone or dolomite and limestone together. Equilibrium studies done by Ding and Olsen[16] concluded that the R ratio strongly influences the SiO_2 activity of the slag and thereby the Si content of the alloy. Iso-activity lines of SiO_2 in the system SiO_2-CaO-Al_2O_3 are shown in Fig 1[18]. The lines representing constant silica activities in the slag are at the same time lines of constant silicon activity in equilibrated metal alloy. From the top apex of Fig 1 are drawn straight lines having constant CaO/Al_2O_3 ratios called R ratios. Thus R ratio is found to be much more important in SiMn production (Eqn. 4) than the lime basicity ratio (Eqn. 3).
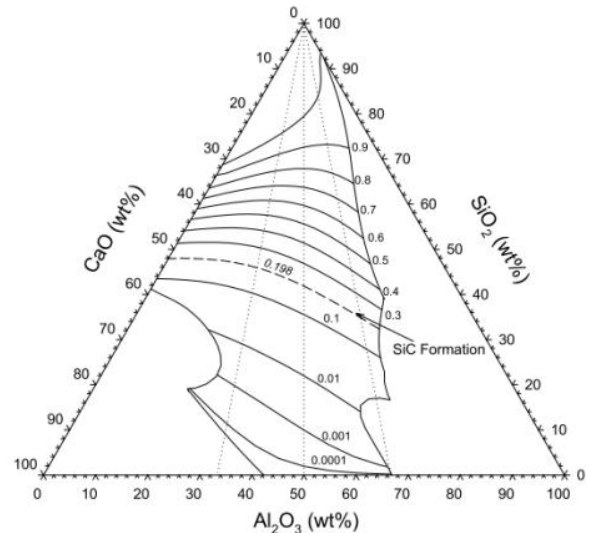

Figure 1. Calculated (FACTSage) iso-activity lines of SiO_2 in SiO_2-CaO-Al_2O_3 slags at 1600 ℃ intersected by lines having constant R ratios (R=CaO/Al_2O_3)[18]
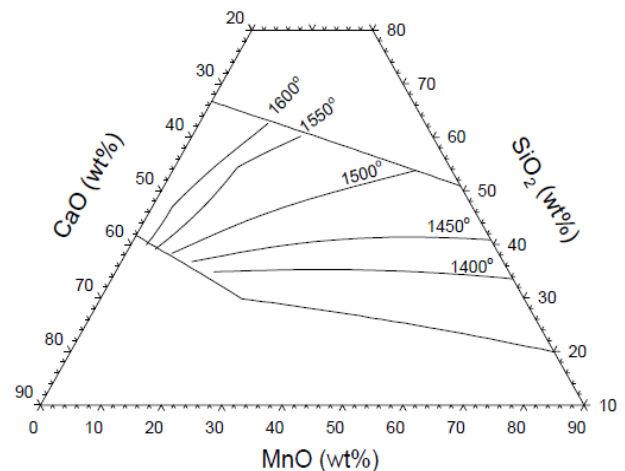
Figure 2. Complete equilibrium relations for ternary MnO-SiO_2-CaO slags in equilibrium with Mn-Si-C_{sat} alloys at P_{CO}=1atm[18]

Fig 2 shows equilibrium relations for ternary MnO-SiO$_2$-CaO slags in equilibrium with Mn-Si-Csat at P$_{CO}$=1 atm. As apparent from Fig 2, equilibrium temperature increase with decreasing MnO content. The liquidus temperature, at which slag is fully liquid, play important role to facilitate reduction reactions. Presence of oxides viz. CaO, MgO, Al$_2$O$_3$ and SiO$_2$ and their mass ratios influence liquidus of slag and thereby control the reduction of MnO and SiO$_2$.

Roghani et al.[19] carried out the equilibrium studies between "MnO"-CaO-(Al$_2$O$_3$+SiO$_2$) slag (at Al$_2$O$_3$/SiO$_2$ weight ratio of 0.55) and Mn-Si alloy (Fig 3). Slag liquidus was found to be inversely related to MnO content of slag at certain CaO%. For example, at 20% CaO in slag, liquidus temperatures were 1680, 1580 and 1475 ℃ for slag containing 10%, 20% and 40% MnO.
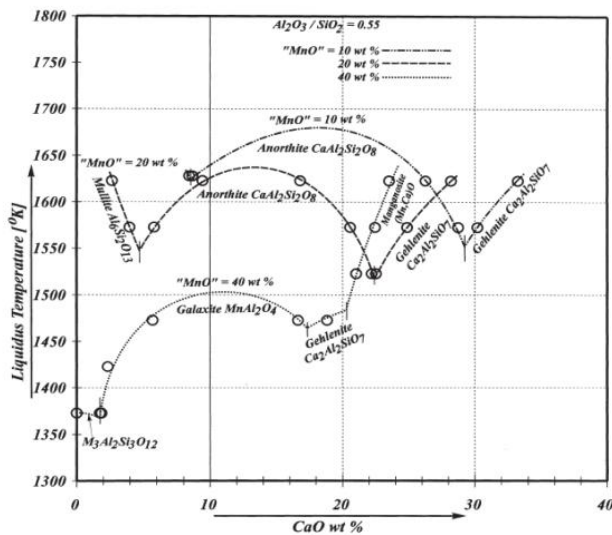

Figure 3. Liquidus in the "MnO"-CaO-(Al$_2$O$_3$+SiO$_2$) system at Al$_2$O$_3$ / SiO$_2$ weight ratio of 0.55 in equilibrium with Mn -Si alloy, as a function of CaO concentration for MnO = 5, 10, 20, and 40 wt pct. Presence of different compounds along the liquidus lines are also shown[19]

Viscosity is one of the fundamental properties of the slag and key parameter for many smelting processes. Viscosity of slag is a complex function of slag composition, temperature and oxygen partial pressure. It is well accounted that the viscosity, being the viscous resistance of the melt in the flow process, prominently relies on the big complex anions (e.g., SiO$_4^{4-}$, Si$_2$O$_7^{6-}$, and Si$_3$O$_{10}^{8-}$) of silica. Hence, the melts will have a high value of viscosity when there is a high SiO$_2$ content such as in the silicomanganese smelting. In absence of external flux i.e. dolomite, the Mn ore and HC-FeMn slag are the source of the CaO, MgO and Al$_2$O$_3$, which form slag upon melting. At this point, the Ca^{2+}, Mg^{2+}, and Mn^{2+} cations are at low concentrations and readily associate with larger ionic groups of silica and thus cause high viscosity. Likewise, a_{MnO} is low at this time due to lower free O^{2-} ions for they are associated by larger silica anions. As the basic oxides contents are increased by addition of dolomite, the Ca^{2+}, Mg^{2+} are increased. The stronger interaction between Ca^{2+}, Mg^{2+} and silicate ions than that between Mn^{2+} and silicate

ions result in stable Ca- and Mg-silicates[20,21]. This give rise to free Mn^{2+} ions which kinetically associate with free O^{2-} ions in the slag and increases a_{MnO} in the slag. The high a_{MnO} in the slag favours the transfer of Mn into metal[8]. In the contrast, a_{SiO2} in slag is diminished by addition of basic oxides and adversely affects the Si content of alloy. Therefore, it is of prime importance to maintain appropriate concentrations of basic oxides as well as silica to yield desired grade of SiMn alloy.

It is always advantageous to simulate the viscosities of equilibrium slags, before proceeding to smelting, to predict slag-metal separation behaviour. A number of semi-empirical models have been developed to estimate the slag viscosities in the case of multicomponent slags[22]. Studies by Muller and Erwee[23] on blast furnace type slags showed that viscosity increased with the basicity of slag at 1500℃ due to formation of solids at high basicities. Studies by Tang and Olsen[24] on MnO-SiO$_2$-CaO-MgO-Al$_2$O$_3$ slag showed that viscosities of liquidus composition at liquidus temperature is of great practical importance.
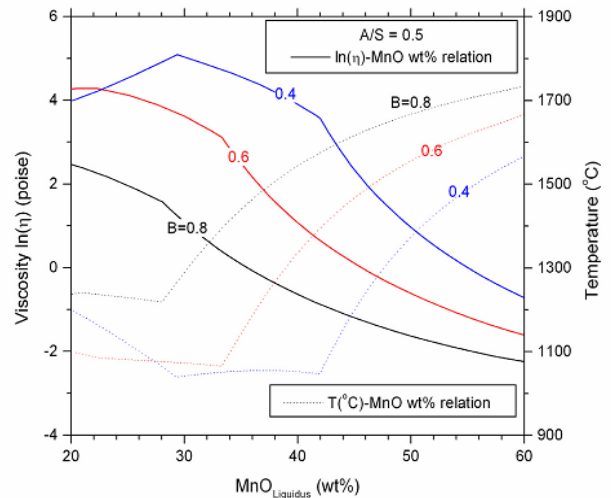

Figure 4. Calculated viscosities along the liquidus with fixed A/S ratio and basicity (solid lines). The dotted lines represent the corresponding temperature in the solid lines[24]

Fig 4 shows the viscosity as function of liquidus MnO content at different slag basicities. The calculated liquidus temperature vs. MnO content relations is shown as dotted lines in the figure. It is evident that an acid slag operation tends to increase the viscosity of "primary liquid slag". The underlying reason is the abundance of SiO$_2$ in acidic slag. The viscosity of pure liquid SiO$_2$ is several orders of magnitudes higher than that of pure alumina and other oxides. Increasing MnO content, on one hand breaks the network and on the other hand increases liquidus temperature, results in the decrease in viscosity of liquid slag. This shows that the viscosity is not "sensitive" to the MnO content.

3. Leached Manganese Nodule Residue Smelting
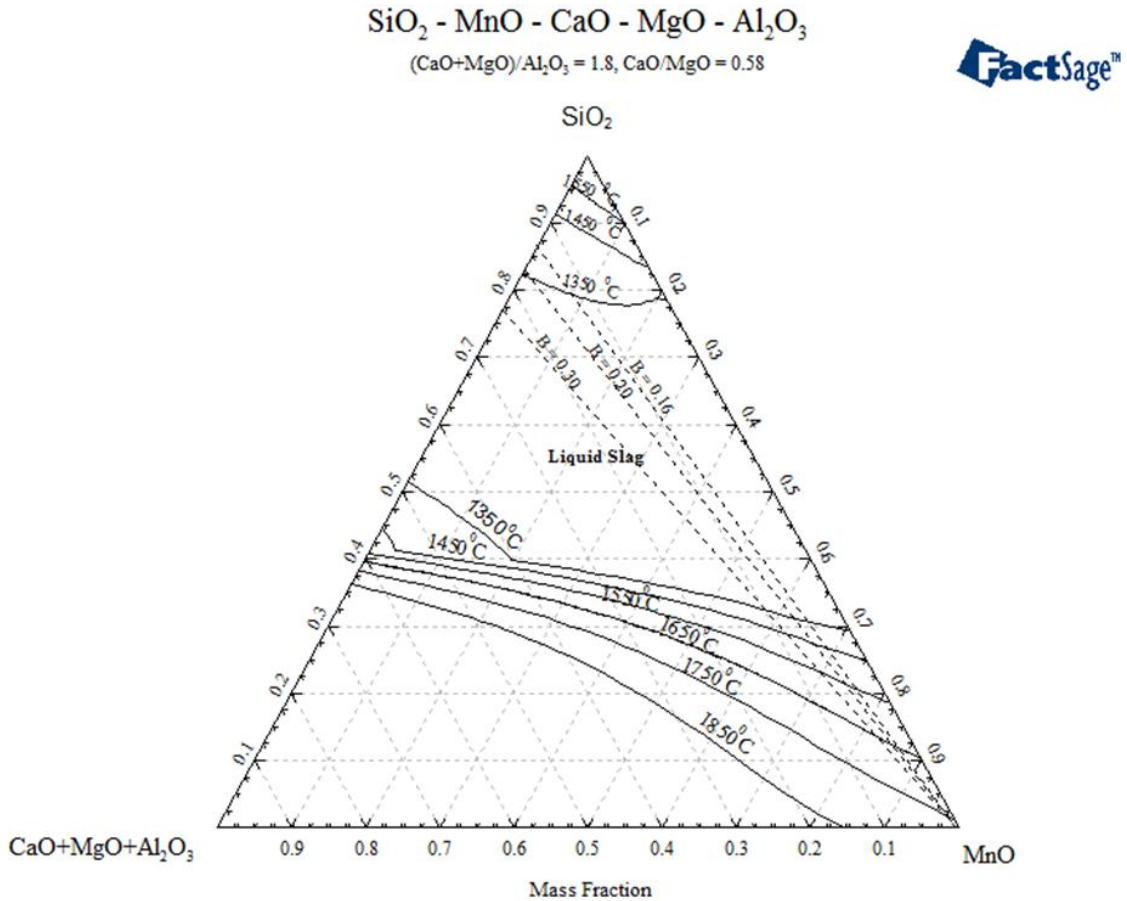
Figure 5. Calculated (FACTSage) Slag-liquid projection at different temperatures for pseudo-ternary slag system (CaO+MgO+Al₂O₃)-SiO₂- MnO, also showing the basicity lines for 0.16, 0.2 and 0.3
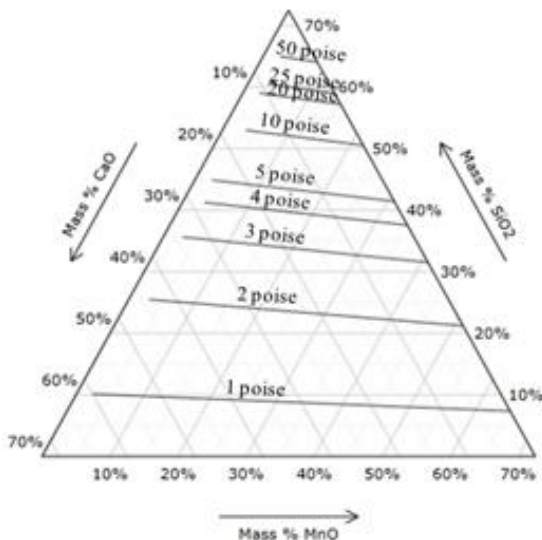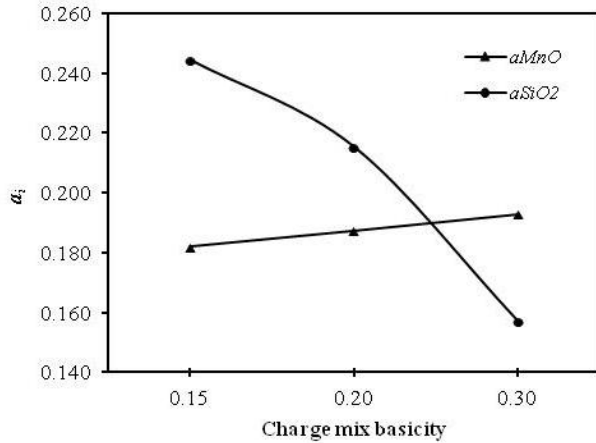

Figure 6. Iso-viscosity line for (CaO+MgO)-(SiO₂+Al₂O₃)-MnO slag system with 12.5 mass % Al₂O₃ and 15 mass % MgO using Urbains model[22]

Earlier paper by present authors[25] reported preparation of various charge mixes containing leached manganese nodules residue (WMNR), Mn ore (MO), quartzite, dolomite, coke etc. and smelting in 50 kVA electric arc furnace to produce standard grade silicomanganese (Si16Mn63, Table 1). The R ratio was fixed at 1.8, which has been reported to be optimum by Eissa et al[5]. The liquidus for CaO-MgO-Al₂O₃-SiO₂-MnO slag system was calculated using FACTSage 6.1 slag database, shown as pseudo-ternary diagram in Fig 5. The fixed basicity lines for 0.16, 0.2 and 0.3 are also drawn. In Fig 5, the liquidus MnO content appears to decrease with the basicity of initial slag. It also appears that slag would contain higher liquidus MnO with increasing Mn/Si at fixed basicity (e.g. B = 0.2) line. From Fig 5, it is apparent that in the lower MnO region (10 wt.%), increase in slag basicity beyond 0.8 give rise to high slag liquidus changing from 1350℃ to 1850℃.

3.1. Role of Charge Basicity in Leached Manganese Nodule Residue Smelting

An increase in the basicity of the slag increases the a_{MnO} (basic oxide) decreases the a_{SiO2} and hence, more MnO and less SiO₂ are reduced with increasing basicity of slag, which is also evident from a_{MnO} and a_{SiO2} of initial slag calculated using Factsage 6.1, shown in Fig. 7. Thus, it is apparent that increasing basicity decreases equilibrium MnO and increases SiO₂ in slag[8]. Therefore, optimum charge basicity is of utmost importance while smelting the MnO and SiO₂ together.

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Figure 7. Calculated a_{MnO} and a_{SiO_2} in the intial slags using Factsage

The optimum charge mix basicity has been found to be 0.2[25], which produced maximum metallic yield and Mn & Si recovery, as shown in Table 1 and Fig.8 (a) & (b) respectively. The standard grade silicomanganese alloy has been produced from charge mix having basicity (B) of 0.2 and 0.3 but basicity of 0.16 produced off-grade with less manganese content (Table 1). The maximum metallic yield (Table 1) and Mn and Si recoveries were obtained at charge 0.2 basicity (Fig. 9 a and b).This can be attributed to the manganese distribution ratio (L_{Mn} i.e. ratio of mass of Mn in slag to that in alloy) on these charge basicities (Fig. 9), which shows sharp decrease with the increase of charge basicity from 0.16 to 0.2, which mean more Mn is transferred to alloy phase. Thereafter, nominal decrease in L_{Mn} was found with charge basicity of 0.3. Thus, charge mix basicity of 0.2 gave rise to better slag composition to yield maximum metallic yield and Mn & Si recovery.

The maximum metallic yield and Mn recovery at charge mix basicity of 0.2 can be explained with the final slag compositions given in Table 2. The slag composition obtained in the smelting of charge basicity 0.16, 2.0 and 3.0 give rise to final slag basicity of 0.50, 0.63 and 0.75, respectively as calculated from Table 2. Increasing charge basicity from 0.16 to 0.2 results in higher reduction of MnO and higher Mn and Si recoveries obtained (Fig. 9 a and b). Increasing charge basicity to 0.3 should have resulted in higher Mn and Si recovery. In contrast, lower metallic yield and manganese recovery with charge basicity 0.3 are obtained, which indicates possible role of insufficient slag fluidity causing less reduction and distribution of Mn and Si between alloy and slag. This is also evident from final slag basicity i.e. 0.75 falling in the higher liquidus region in Fig. 5. Thus, presence of solids in the final slag obtained from smelting of charge with basicity 0.3 produced lower recoveries and yield.

Table 1.   Comparison of alloy composition obtained from smelting of charge mixes at different basicity with target silicomanganese grade (Si16Mn63)

Sl no./ Grade	Initial Charge basicity	% Metallic yield	%, by mass					
			Mn	Si	C	S	P	Fe
Si16Mn63	----	----	60-65	14-17	2.5 max.	0.03 max.	0.3 max.	balance
1	0.16	63.41	58.14	15.72	2.10	0.025	0.26	22.85
2	0.2	73.37	61.27	17.66	1.9	0.016	0.12	17.81
3	0.3	62.14	61.71	14.49	2.34	0.014	0.12	19.75

Table 2.   Chemical composition of slags obtained from smelting of charge mix with different basicities

Initial Charge basicity	%, by mass						Final slag basicity
	CaO	MgO	Al_2O_3	SiO_2	MnO	FeO	
0.16	9.25	12.20	18.25	42.80	16.75	1.20	0.50
0.20	10.14	16.08	19.38	41.75	11.66	0.4	0.63
0.30	13.29	18.39	17.63	42.22	6.57	0.89	0.75
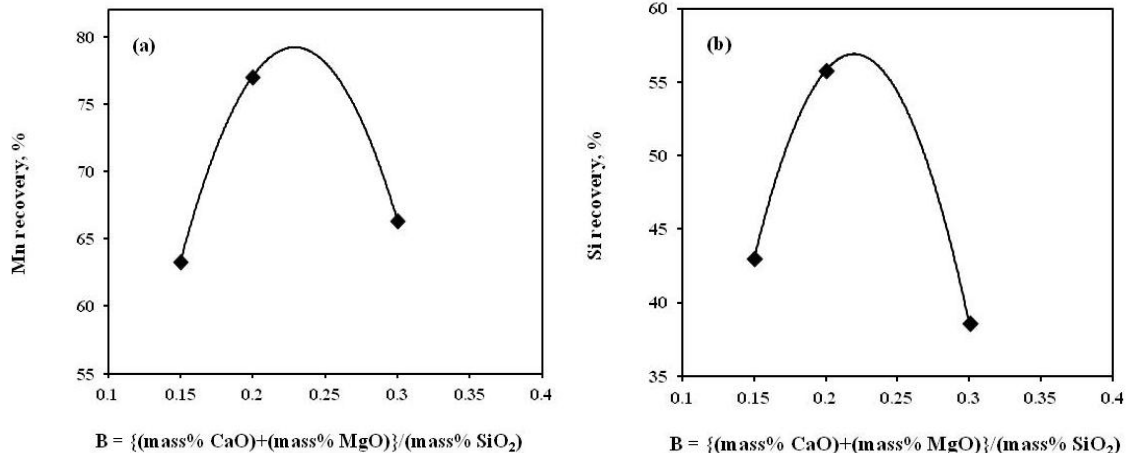
Figure 8.   Effect of charge mix basicity on recovery of (a) Mn and (b) Si in alloy
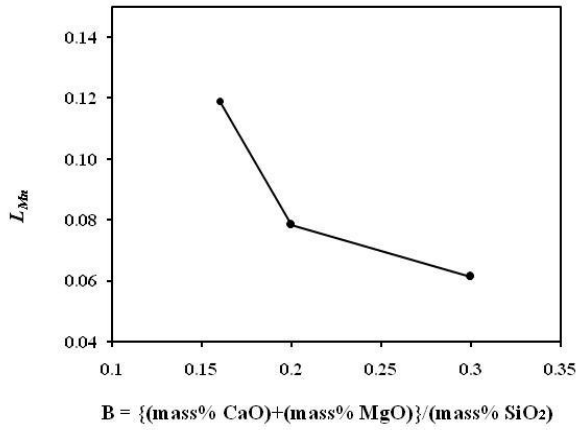
Figure 9. Effect of charge mix basicity on Mn distribution between slag and alloy

3.2. Effect of CaF₂ Addition

The chemical composition of alloys obtained from CaF_2 addition smelting trails are given in Table 3. The acidic slag in silicomanganese s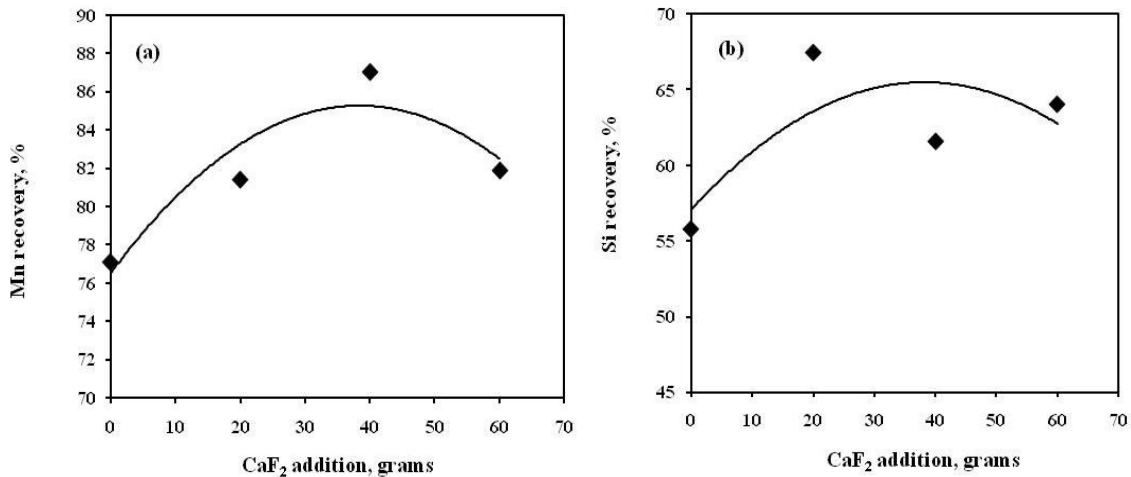melting often poses difficulties in slag-alloy separation leading to lower yield and recovery. Therefore, CaF_2 is often added in the acidic slag to decrease the viscosity. The CaF_2 breaks the SiO_2 network in the slag and improves slag fluidity. On the other hand, dissolution of CaF_2 in the slag give rise to more CaO, which increases slag basicity as well as slag liquidus. Therefore, optimum amount of CaF_2 must be ascertained before proceeding to commercial smelting trials. The CaF_2 addition made in molten charge at initial charge mix basicity of 0.2, during holding time, found to be beneficial for smelting yield and recoveries. The Mn recovery (Fig. 10(a)) increased with addition of CaF_2 up to 4% of WMNR:MO blend but resulted in decreasing Mn recovery with 6% CaF_2 addition. The Si recovery (Fig. 10(b)) has also been found to increase with addition of 2% CaF_2 and thereafter decreased with further addition of CaF_2. The decreasing manganese distribution ratio (L_{Mn}) has been obtained up to 4% of CaF_2 addition (Fig. 11), which depicts the proper slag metal separation. Addition of 6% CaF_2 showed increased manganese distribution ratio (L_{Mn}).

Table 3. Chemical compositions of alloys and metallic yield of smelting trials carried out with varying addition of CaF₂ during holding period

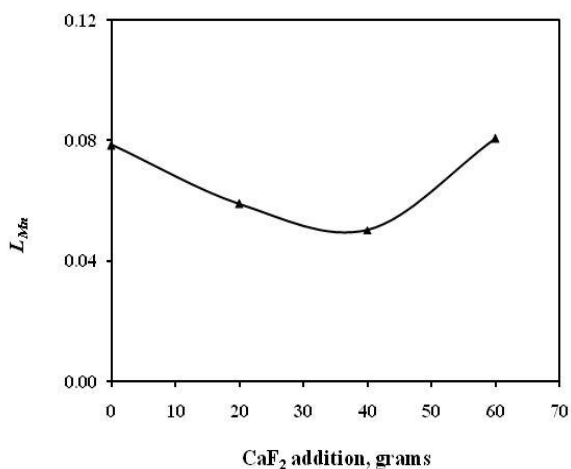| Designation	CaF₂, grams	% Metallic yield	%, by mass					
			Mn	Si	C	S	P	Fe
Si16Mn63	----	----	60-65	14-17	2.5 max.	0.03 max.	0.3 max.	balance
1	0	73.37	61.27	17.66	1.9	0.015	0.12	17.81
2	20	78.45	60.77	20.07	1.48	0.0043	0.14	16.6
3	40	81.86	61.88	17.44	2.08	0.021	0.12	17.39
4	60	79.67	59.8	18.64	2.07	0.0075	0.13	18.49

Table 4. Chemical composition of slags obtained from smelting of charge mix with different CaF₂ additions

CaF₂ addition (% of WMNR+ MO)	%, by mass						Final slag basicity
	CaO	MgO	Al₂O₃	SiO₂	MnO	FeO	
2.0	14.29	15.19	17.07	39.94	13.45	0.97	0.73
4.0	16.10	13.25	15.19	38.49	12.97	0.72	0.76
6.0	20.04	12.56	14.88	39.97	9.38	0.43	0.82

Figure 10. Effect of CaF₂ addition on recovery of (a) Mn and (b) Si in alloy

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Figure 11. Effect of CaF$_2$ addition on Mn distribution between slag and alloy

Though Mn distribution ratio (L_{Mn}) increased with CaF$_2$ addition, lower metallic yield and Mn and Si recoveries were obtained at 6% CaF2 addition. This may be may be attributed to increase in final slag basicity due to increasing CaO content in slag, as shown in Table 4. Further addition of CaF$_2$ i.e. 6% increased the slag basicity to 0.82, which has very high liquidus (>1850℃) as shown in Fig 5.

4. Conclusions

Smelting studies have shown that leached manganese nodule residue (WMNR) is a potential raw material for producing standard grade silicomanganese alloy (Si16Mn63). The thermodynamics and viscosity aspects of silicomanganese smelting have been evaluated and applied to WMNR smelting. The higher metallic yield and Mn recoveries at charge mix basicity of 0.2 were satisfactorily correlated to slag liquidus calculated using software Factsgae. Addition of CaF$_2$ up to 4% of WMNR+Mn ore blend during holding time was found to be beneficial to metallic yield and Mn recovery. Further CaF$_2$ addition increased the slag liquidus resulting in lower metallic yield and Mn and Si recoveries. Thus thermodynamic and viscosity studies of WMNR smelting has been found to be useful for charge mix optimisation and maximisation of metal recovery in the production silicomanganese from manganese nodules leached residue.

ACKNOWLEDGEMENTS

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