Production of Fe-Si-Mn from leached sea nodule residue

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ABSTRACT: A pilot plant for processing of polymetallic sea nodule on 500 Kg/day scale has been set up by Department of Ocean Development at CRDL, HZL, Udaipur. After recovery of Cu, Ni & Co by NH_3/SO_2 pressure leaching, the generated residue contains considerable amount of manganese and iron. Attempts on recovery of manganese from this residue has been made at National Metallurgical Laboratory and standard grade Fe-Si-Mn alloy has been produced. Two different routes of smelting were carried out which comprised single stage smelting of residue blended with manganese containing materials and two stage smelting of residue with out any blending. The process is developed at 20 Kg scale and has been tested at 300 Kg scale in pilot plant also. A maximum recovery of Mn in the form of Fe-Si-Mn alloy has been found 68.0%.

1 INTRODUCTION

The sea nodules are rock concentrates on the sea bed sediments formed by concentric layers of iron and manganese hydroxide around a core. Metal entities such as Cu, Ni, Co, Mo & Zn are accommodated in the complex cage of iron and manganese hydroxides. So far, several processes have been developed for extraction of Cu, Ni & Co from sea nodules which combinedly constitute less than 2.5% by weight and almost 70% of the weight of the nodule may result in leach residue. The residue contains mainly manganese (22%), iron (10%), silicon (8%), alumina (4%) and magnesia (4%) besides several other minor and trace elements, which can be subjected for production of Mn alloys such as ferro-silico-manganese. Furthermore, disposal of such a large amount of very fine solid residue may create the environmental as well as waste management problems. Therefore, it was envisaged to recover manganese and iron in the form of ferro-alloy viz. Fe-Si-Mn from leached sea nodule residue. The ferro-silico-manganese alloy is extensively used in the steel industry as deoxidising and alloying material. The present paper throws light on the studies carried out for the recovery of manganese metal from leached sea nodule residue by smelting route.

2 EXPERIMENTAL

2.1 Materials and methods

The leached sea nodule residue generated after leaching of Cu, Ni & Co by Ammonia/Sulphur dioxide route at sea nodules processing pilot plant of DOD at HZL, Udaipur, has been used for the present studies. The typical composition of as received leached sea nodule residue, blending materials, reductant and fluxes are given in Table- 1 & 2.

Table - 1: Composition of leached sea nodule residue from HZL, Udaipur

Const.	%	*Const.*	%
Mn	22.60	S	3.48
Fe	10.49	P	0.15
Si	8.64	NH_4^+	1.60

Table - 2: Chemical composition of blending materials, reductant and fluxes

Fe-Mn Slag	MnO – 35.5% FeO - 0.80 %
Mn Ore	MnO_2 – 49.0 % Fe_2O_3 – 10.0 %
Electrolytic Mn metal	Mn – 99.90 %
Coke	Fixed carbon – 77.0 %
Quartz	Silica – 92.0 %
Limestone	CaO – 49.0 %

Washing of as received leached residue was carried out for the removal of sulphate and ammonia, in a open tank fitted with mechanical stirrer and other necessary attachments. The residue was mixed with plain water in the Solid: liquid ratio of 1:10. The residue slurry was agitated for 1.0 hors at 40 rpm and then filtered by a filter press. The filtered residue was dried at 100^{o}C for 3 hours and mixed with binder i.e. bentonite (2.0 % by weight) and pellets of 5-12 mm size were prepared on disc peletiser with appropriate amount of water. The pellets were dried before preparing charge mix.

In blending type experiments, charge mix was prepared by mixing certain quantity of blending materials (Fe-Mn slag, Mn ore or Mn metal) with residue pellets. In the blended residue resulting grade of Mn and Mn/Fe ratio is given in the Table-3.

Table- 3: Grade of blended charge

Blending material	Resiude: Blended material	Resulting grade	
		Mn/Fe ratio	Grade of Mn (%)
Fe-Mn Slag	1:1	3.8:1	26.6
Mn Ore	1:0.7	3.5:1	35.3
Mn metal	1:0.2	3.6:1	37.5

The blended charge was mixed with required quantity of coke and flux which was subjected to smelting.

In the two stage smelting experiments, the first stage charge comprised of residue pellets mixed with calculated amount of coke and quartz. This charge was smelted in the same furnace. The 1st stage alloy was tapped after sufficient time of smelting and molten slag was allowed to remain inside the furnace. The second stage charge which contained coke and lime stone was added in the 1st stage molten slag and proper time was given for complete reactions. Both the alloy and slag were tapped out at the end of smelting.

3 RESULTS AND DISCUSSION

3.1 Washing of leached residue

The chemical composition of washed residue is given in Table-4, which shows a significant decrease in the sulphur content of the residue. The washing of residue is necessary due to the fact that higher amount of sulphur in raw material may alter the desired composition of final product i.e. Fe-Si-Mn whereas ammonia in residue likely to create environmental problem upon smelting.

Table-4: Chemical composition of unwashed & washed residue

Const.	Unwashed residue	Washed residue
% Mn	22.20	25.46
% Fe	8.98	12.41
% Si	7.53	10.08
% S	3.38	0.35
% P	0.15	0.17
% NH_4^+	1.60	0.25

In all the smelting experiments, washed residue was used for charge preparation and subsequent smelting.

3.2 Smelting of washed residue blended with Fe-Mn slag/ Mn ore/ Mn metal

For the production of standard grade Fe-Si-Mn, the raw material should necessarily have sufficiently high Mn/Fe ratio (1) whereas the sea nodule residue has Mn/Fe ratio of 2:1, which was improved by blending it with materials such as Fe-Mn slag, Mn ore or electrolytic Mn metal. Typically, charge composed of appropriate amounts of washed residue pellets, blending material, reductant and fluxes. The charge was smelted in 50 KVA submerged arc furnace on 10 Kg residue pellets per batch. The furnace was of rectangular shape and lined with mag-carbon bricks. The temperature of the melt was kept around 1650^{o}C as the reduction of manganese and silicon dioxides (Habashi; Riss and Khodororovsky, 1967) are feasible only around 1400-1500^{o}C and 1550^{o}C respectively. A reaction time of 30 min. was provided after complete melting of charge. The power input maintained during smelting was 700 Amps and 70

Volts. A typical composition of Fe-Si-Mn alloy produced in smelting experiment with blended charge given in Table-5.

Table - 5: Typical composition of Fe-Si-Mn alloy produced with blending

Radical	*%*	*Radical*	*%*
Mn	63.40	C	1.5
Fe	18.17	S	0.03
Si	15.90	P	0.17

Recoveries of manganese by smelting with charge containing Fe-Mn slag, Mn ore & Mn metal were found as 35.86 %, 53.40 % & 57.73 respectively. A comparison of smelting with three blending materials is given in Table-6.

Table-6: Comparison of smelting with three different blending materials

Parameter	Fe-Mn Slag	Mn Ore*	Mn Metal
Recovery of Mn	35.86 %	53.4 %	57.73 %
Slag/Metal ratio	4.93:1	2.01:1	0.96:1
Power (kWh per *kg of alloy)*	17.5	10.5	8.75
Smelting Time	90 min.	90 min.	60 min.

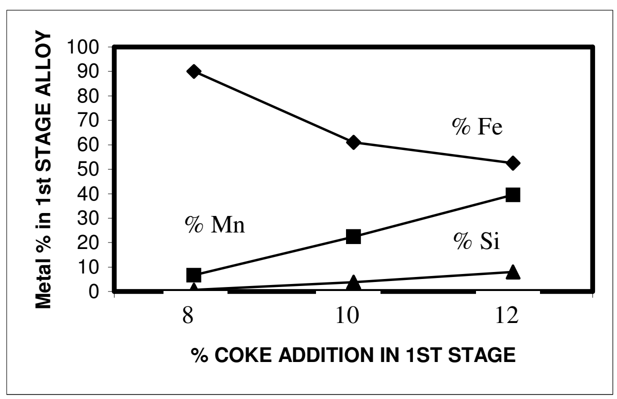
It is apparent from the table that the higher slag-metal ratio requires higher input of power. The recovery of Mn with Fe-Mn slag is low which can be attributed to higher slag-metal ratio as well as the metal entrapment in the slag phase. Other factors for low manganese recovery in alloy were low charge bed height compared to industrial practice and escape of fumes during smelting. However, the above comparison exhibits that smelting of residue with blending of Mn ore is quite encouraging. Use of Mn metal as blending material would costly proposition.

3.3 Two stages smelting of washed sea nodule residue

Smelting in two stages was also applied successfully to produce Fe-Si-Mn from washed residue. In this process, first stage smelting of residue with limited amount of coke was carried out for selective reduction of iron oxide and tapping of iron rich alloy leaving molten Mn rich slag in the furnace. The Mn rich slag can be subjected to further smelting for producing standard grade Fe-Si-Mn alloy (Gabdullin et al, 1992). In second stage smelting of 1st stage molten slag with sufficient amount of coke and flux was carried out to produce standard grade Fe-Si-Mn alloy.

According to the free energy data of carbothermic reduction of iron, manganese and silicon oxides, the sequence of reduction is iron oxide, manganese dioxide followed by silicon dioxide. In this view, limiting the quantity of coke can control the reduction reactions in the bath. Hence, the amount of coke in the first stage smelting plays an important role, which is evident from the figure-1. As the amount of coke is decreased from 12.0% to 8.0% of residue weight, the percentage of manganese and silicon decreased while that of iron increase in the alloy phase.

Figure 1: Relation between amount of coke and metal in alloy phase



Consequently, the slag became rich in manganese and silicon oxides and Mn/Fe ratio became higher

In the second stage, an excess amount of coke (~ 30% of slag weight) along with 40% limestone added into the molten slag. Since the reduction of manganese & silicon oxides require high temperature, relatively high power input was maintained during 2nd stage of smelting as compared to that for 1st stage smelting. Furthermore, low temperature produces carbides of Mn & Si, which can increase the viscosity of slag resulting in decrease of reduction velocity. The higher viscosity may also decrease the recovery of manganese due to metal entrapment in slag.

The % Mn recovery in Fe-Si-Mn alloy in 2nd stage for addition of 8%, 10% and 12% coke addition in 1st stage was found 51%, 61% & 68% respectively.

3.4 Evaluation of Fe-Si-Mn alloy produced from smelting of residue

In order to evaluate the suitability of Fe-Si-Mn produced as deoxidiser in steel melting, two heats were made at Tata Steel. Heat no. 1A was produced with standard silico-manganese where as heat no. 2A was produced with silico-manganese produced from sea nodule residue. The chemical analyses of these samples are given in Table – 7

Table - 7 Chemical compositions of steel ingots

S. No.	*%C*	*%Mn*	*%S*	*%P*	*%Si*
1A	0.28	0.54	0.012	0.023	0.28
2A	0.21	0.52	0.012	0.023	0.20

Both the ingots were homogenised at 1000^0C, then forged and rolled. The hardness of sample 1A & 2A was found to be 233 and 201 respectively on VHN scale whereas the tensile strengths were 585 MPa and 599 MPa respectively. The lower hardness value for specimen produced 2A is due to low carbon content in the steel (0.21 against 0.28).

4 CONCLUSION

Standard grade silicomanganese can be produced by smelting of residue blended with Fe-Mn slag/ Mn ore or Mn metal. The two stages smelting of washed residue pellets without addition of any manganese containing material produced standard grade Fe-Si-Mn alloy. To evaluate the techno-economic feasibility of the processes mentioned above more tests on higher scale is necessary. For this NML has set up a 350 Kg/day sea nodule residue processing plant for the production of Fe-Si-Mn alloy.

5 REFERENCES

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