Rich manganese slag from refined ferromanganese is poured into a shaking ladle, and liquid silicomanganese is added. By shaking for 10 minutes, the manganese content of the slag can be reduced from 18 to 4.8 per cent, and the silicon content can be decreased from 19.0 per cent to 11.6 per cent. By the use of low-silicon (11.6% Si) silicomanganese and the addition of lime and manganese ore, refined ferromanganese can be produced. The consumption of silicomanganese in this production of refined ferromanganese is 920 kg/t, and the manganese recovery is about 80 per cent.

**Historical Review**

Before 1980, the converter method was tried for the production of refined ferromanganese (FeMn). Refined FeMn can be obtained by the decarburization of liquid high-carbon FeMn in a converter by means of oxygen blowing. Because of the high SiO₂ content of Chinese manganese ores, they are suitable for the production of silicomanganese (SiMn) but not for the production of FeMn. SiMn is normally used as a raw material for the production of refined FeMn.

The old method, as this is known, proceeds as follows. Cold (at room temperature) manganese ore and lime are smelted together in a refining furnace. When the silicon content in the metal bath is less than 2.5 per cent, the smelting process can be considered to be finished and the liquid alloy can be tapped.

The desiliconization reaction is

$$2\text{MnO} + \{\text{Si}\} = 2\text{Mn} + \{\text{SiO}_2\},$$

where the round and square brackets refer to the slag and metal phases respectively.

The shortcomings of this method are the high consumption of electrical energy (about 2000 kWh/t) and the low recovery (about 60 per cent) of manganese.

**The Current Process**

In an attempt to increase profits, a new process for the production of refined FeMn was begun on an experimental basis in 1979. A flow-chart of the process is shown in Figure 1.

After a heat of refined FeMn was completed in the refining furnace, the liquid alloy was poured into ingot moulds, and the slag into the shaking ladle. The composition of the slag was as follows (in percentages by mass):

- MnO: 23%
- CuO: 39%
- SiO₂: 27%
- MgO: 4%
- Al₂O₃: 5%

The weighed SiMn from the submerged-arc furnace was then poured into the shaking ladle and shaken for 10 minutes. When the manganese content of the slag had dropped to 5 per cent, the slag was discarded. Owing to the desiliconization reaction in the shaking ladle, the SiMn turned into an intermediate product – low-silicon (11.6 per cent Si) Si–Mn alloy.

The composition of the slag and alloy before and after shaking are shown in Table I.

<table>
<thead>
<tr>
<th>Slag 1</th>
<th>Intermediate Si–Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO 23%</td>
<td>Si 11%, Mn 73%</td>
</tr>
<tr>
<td>Slag 2</td>
<td>FeMn</td>
</tr>
<tr>
<td>Mn &lt; 5%</td>
<td>FeMn (Si &gt; 17%)</td>
</tr>
</tbody>
</table>

FIGURE 1. Flow chart for the shaking-ladle refining method for the production of refined ferromanganese.

1. Slag 1: Slag of unrefined FeMn before shaking.
2. Slag 2: Slag of refined FeMn after shaking.
TABLE I
COMPOSITION OF SLAG AND ALLOY BEFORE AND AFTER SHAKING

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition of alloy, %</th>
<th>Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Si</td>
</tr>
<tr>
<td>Before shaking</td>
<td>66,50</td>
<td>19,0</td>
</tr>
<tr>
<td>After shaking</td>
<td>73,24</td>
<td>11,64</td>
</tr>
</tbody>
</table>

The new process for the production of refined ferromanganese was adopted in 1984 at another plant. Statistical analyses of the results of more than 600 heats are shown in Table II and Figures 2 and 3.

TABLE II
BENEFITS OF THE NEW PROCESS

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy consumption kWh/t</th>
<th>Recovery of Mn %</th>
<th>Consumption of SiMn kg/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old</td>
<td>1883</td>
<td>61,34</td>
<td>1050</td>
</tr>
<tr>
<td>New</td>
<td>823</td>
<td>80,02</td>
<td>920</td>
</tr>
</tbody>
</table>

Factors affecting the MnO content of slag 2, such as its basicity, the silicon content of the Si–Mn alloy, the silicon content of the intermediate Si–Mn alloy, the apparent equilibrium constant, the shaking speed, and the shaking time, are given in detail elsewhere.

The relationship between the MnO content of slag 2 and the basicity, B₂, of slag 1 is shown in equation [2] and Figure 2.

\[
\text{(%MnO)} = 21,45 - 14,05 \, B₁ - 0,1 \, B₁^2 + 1,6 \, B₁^3 [2]
\]

where

\[
B₁ = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_₂}.
\]

Figure 2 shows that, as the basicity, B₁, increases, the MnO content of slag 2 decreases. When the basicity is greater than 1,6, the desiliconization reaction hardly occurs and the optimum basicity of slag 1 is 1,35 to 1,5.

When the reaction has reached equilibrium after shaking, the MnO content of slag 2 depends on the silicon content of the intermediate alloy and the basicity of slag 2, B₂. The relationships between these parameters are shown in equations [3] and [4] and Figure 3.

When 11% < [\%Si] ≤ 12%,

\[
(\%\text{MnO}) = 29,67 - 37,24 \, B₂ + 14,35 \, B₂^2 [3]
\]

When 12% < [\%Si] ≤ 13%,

\[
(\%\text{MnO}) = 36,63 - 48,19 \, B₂ + 18,14 \, B₂^2 [4]
\]

Figure 3 shows clearly that, with an increase in the basicity, B₂, and silicon content of the intermediate alloy, the MnO content of slag 2 falls but, when the basicity B₂ is more than 1,3, the fall in the MnO content becomes insignificant.
The apparent equilibrium constant of equation [1] is given by

\[ K_b = \frac{[%Mn]^2}{(%SiO_2)/(%MnO)} \cdot [\%Si] \]

\( K_b \) is an important parameter: the greater the value of \( K_b \), the more the reaction goes to completion. According to the literature, both temperature and slag basicity influence the apparent equilibrium constant, but the influence of basicity is greater. After computer processing of the production data, the following relationship between \( B_2 \) and \( K_b \) was obtained:

\[ K_b = -3358 + 6005.1 \cdot B_2 - 1920.5 \cdot B_2^2 - 250.6 \cdot B_2^3 \]  
\[ \text{[5]} \]

Equation [5] shows that \( K_b \) increases as the value of \( B_2 \) increases. When \( B_2 \) reaches a critical value, the value of \( K_b \) drops, owing to the increase in the melting point of the slag and the resulting increase in the slag viscosity.

The optimum value of \( B_2 \) is 1,10 to 1,26. The optimum shaking speed is about 45 r/min and the optimum shaking time is 10 minutes. It was found that the silicon content of the Si-Mn alloy had a slight influence on the MnO content of slag 2.

The new process has the following advantages over the old process.

1. The desiliconization addition in the furnace is lower. Only 10 per cent of the silicon is reduced in the new process, compared with more than 15 per cent in the old process.
2. Less lime is needed. Because of the decrease in the necessary desiliconization addition, the lime addition for slagmaking can be decreased, and therefore the volume of slag, the power consumption, and the manganese in the slag can also be decreased.
3. Liquid low-silicon Si-Mn alloy can be used, and no energy is needed to remelt the solid Si-Mn alloy.
4. There is less residual manganese in slag 2. The residual manganese content of the final slag decreased from 18 to 4.8 per cent.

The new technology for the production of medium and low-carbon FeMn is widely used in China.

The Future

In order to further decrease the consumption of SiMn and increase the manganese recovery, Liaoyang Ferroalloy Plant, using rich manganese slag of high-carbon FeMn for the production of refined FeMn, has developed this process a stage further.

The fourth workshop of Liaoyang Ferroalloy Plant previously had two submerged-arc furnaces. Furnace No. 1, with a capacity of 12.5 MVA, produced SiMn, and Furnace No. 2, with the same capacity, produced high-carbon FeMn using fluxless operation. The slag from the high-carbon FeMn operation contained up to 30 per cent manganese and was used to produce SiMn after being cooled.

In 1988, a new 3.5 MVA electric refining furnace, Furnace No. 3, and a shaking ladle were installed to produce high-quality refined FeMn from high-manganese slag. Two different processes are used, depending on the availability of electrical power.

1. When the power supply is not adequate for production, Furnace No. 2 is stopped and the submerged-arc Furnace No. 1 and refining Furnace No. 3 are combined in the new process (Figure 1).
2. When there is sufficient power, the second process will be put into operation, which is the combination of three furnaces into one process as follows. Furnace No. 2 produces high-carbon FeMn by fluxless operation. The slag, which contains 30 per cent manganese, is poured into Furnace No. 3 to replace part of the manganese ore in the production of refined FeMn, and the other operations are the same as those in the first process.

The manganese ore used for the production of refined FeMn contains high-valency iron and manganese oxides (as MnO₂, etc.). A large amount of silicon is needed for the reduction of these oxides, which also causes an increase in the slag volume. In the production of refined FeMn from high-manganese slag instead of manganese ore, a large amount of silicon can be saved because of the absence of high-valency iron and manganese oxides and a lower amount of FeO. Therefore, the consumption of Si-Mn alloy can also be decreased.

In 1991, Liaoyang Ferroalloy Plant enlarged the volume of the shaking ladle from 4.5 to 8 m³, so that larger batches of slag could be processed.

The total energy consumption during the production of refined FeMn consists of energy consumed to produce Si-Mn alloy and refined FeMn. The energy consumed in the production of Si-Mn alloy is about 85 per cent of the total energy consumed in the production of refined FeMn. Furthermore, the cost of Si-Mn alloy constitutes about 75 per cent of the production cost of refined FeMn. Therefore, the main aim of decreasing both the power consumption and the cost of refined FeMn alloy is to decrease the consumption of Si-Mn alloy.

The use of liquid high-manganese slag instead of manganese ore to produce refined FeMn is an effective way to save energy and lower the cost of production.

Conclusions

1. By means of the new ladle-refining technology, power consumption can be reduced from 1883 to 823 kWh/t, the manganese recovery can be increased from 61.34 to 80.02 per cent, and the consumption of silicomanganese can be decreased from 1050 to 920 kg/t.
2. Since the additions of manganese ore and lime can be adjusted, a balance can be obtained between the processes in the shaking ladle and the refining furnace.
3. Owing to the low siliconmanganese consumption and high manganese recovery, the economics of the process are highly favorable.

References
