Desulphurisation Process in RH Degasser for Soft-killed Ultra-low-carbon Electrical Steels

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This study introduces the desulphurisation process in RH (Vacuum Recycling Degassing) degasser developed for the soft-killed ultra-low-carbon electrical steels. A CaO–Al₂O₃–CaF₂–based desulphuriser with high sulphide capacity was developed by laboratory experiments of steel desulphurisation and by considering the floatation of Al₂O₃ (the deoxidation product). The optimum composition of the desulphuriser was found to be mass%CaO/mass%Al₂O₃=2.5–4, SiO₂<5% and F⁻<8% with the melting point lower than 1350°C. To prevent the resulphurisation of steel, the effect of components in the top slag on sulphur partition between slag and steel was calculated using the thermodynamic package FACTSAGE and the range of the components in the top slag was proposed to control the oxygen potential. It was found that FeO+MnO content in the top slag should be controlled below 15% before RH and 10% after RH degassing treatment. Industrial trials were carried out by controlling the FeO+MnO content in the top slag via slag modification and adding RH desulphuriser after final deoxidation. The results from industrial trials showed that resulphurisation was effectively prevented by controlling the FeO+MnO content in top slag below 15% via slag modification. The combination of the top slag modification and the addition of RH desulphuriser consistently produced the ultra-low-carbon steel with sulphur content less than 0.005%.

KEY WORDS: RH desulphurisation; sulphur partition; desulphuriser; ultra-low-carbon electrical steel; soft-killed; sulphide capacity.

1. Introduction

Sulphur content and sulphide inclusions in the steel, which have strong impacts on the steel quality, are important indicators of steel cleanliness. The electrical steels have strict requirement of sulphur content, because sulphur is harmful to magnetic properties in ultra-low-carbon electrical steel, which can suppress the grain growth and increase magnetic hysteresis loss, especially for high grade electrical steel. So sulphur content in electrical steels should be controlled below 0.005%.

In a steel plant the BOF (Basic Oxygen Furnace)-LF (Ladle Furnace)-RH (Vacuum Recycling Degassing)-CC (Continuous Casting) process route is employed to produce ultra-low-carbon electrical steels and the composition is shown in Table 1. During vessel tapping, the steel is not deoxidised or only partially deoxidised by adding ferromanganese alloys (“soft-killed”) instead of completely killed steel produced by adding aluminum as in the traditional process. The advantages of the soft-killed process are that, the deoxidants added during tapping can be eliminated and high oxygen content in the steel can be used to remove carbon in RH, and subsequently the production cost can be reduced. The amount of oxide inclusions in the steel can also be reduced effectively due to the elimination of deoxidation during tapping. However, in ladle furnace (LF), desulphurization is not effective and resulphurisation is likely to happen due to the high oxygen content in steel and slag, and so LF is only used to increase temperature in this plant. Desulphurisation is performed in RH after decarbonation, deoxidation and alloying process, and it is restricted to be finished in 6–10 minutes due to the restriction of production rhythm. Reducing atmosphere and slag with high sulphide capacity are thermodynamically needed to realize deep desulphurisation. However, because of the adoption of the soft-killed process during vessel tapping, the FeO+MnO content in top slag is high which may reduce the effectiveness of the RH desulphuriser added and results in resulphurisation of steel. Although hot metal pretreatment is performed to lower S to below 0.003%, [S] in steel after tapping was still higher because of sulphur brought by other raw materials, e.g. scrap, residual desulfurized slag, lime and composite slag. Therefore, controlling FeO+MnO content in top slag and developing a RH desulphuriser with high sulphide capacity are the keys to producing ultra-low carbon and sulphur electrical steels via soft-killed process.

In this study, the desulphuriser in RH degasser was first investigated by laboratory steel desulphurisation experiments and by considering the floatation of Al₂O₃ (the deox-

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Table 1. Composition of Electrical Steel.

<table>
<thead>
<tr>
<th></th>
<th>(mass%)</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>≤0.005</td>
</tr>
<tr>
<td>Si</td>
<td>0.45–0.75</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15–0.50</td>
</tr>
<tr>
<td>Sol.Al</td>
<td>0.15–0.35</td>
</tr>
<tr>
<td>S</td>
<td>≤0.005</td>
</tr>
<tr>
<td>P</td>
<td>0.01–0.03</td>
</tr>
</tbody>
</table>
idation product). Then the effect of top slag compositions (FeO+MnO content, mass%CaO/mass%Al₂O₃ ratio, MgO content and SiO₂ content) on sulphur partition between slag and steel has been studied using the thermodynamic package FACTSAGE and optimal FeO+MnO content in the top slag has been determined to prevent the resulphurisation. Finally industrial trials were carried out by controlling the FeO+MnO content in the top slag via slag modification and adding RH desulphuriser after deoxidation, and the sulphur level in the end product was consistently reduced to below 0.005% to meet the product requirements.

2. Laboratory Investigation on RH Desulfuriser

2.1. Experimental Study

The desulphuriser used in RH degasser is generally added by either powder injection or via vacuum pipe. It is added through vacuum pipe in plant trials. The main desulphurisers for RH desulphurisation are based on CaO–CaF₂ and CaO–Al₂O₃–CaF₂⁵–⁹) and in this work the latter was investigated. Seven groups of desulphurisers were designed, as shown in Table 2, with varying CaO/Al₂O₃ ratio or CaF₂ content. The sulphur partition ratio between slag and steel (LS = mass% (S)/mass% [S]) was studied by laboratory desulphurisation experiments.

The experimental setup was shown schematically in Fig. 1. Cylindrical steel samples (40 mm in diameter and 40 mm in height) were prepared from electrical steel with initial sulphur content of 0.0092%. The steel sample and pre-melted slag (Table 2) were put into an MgO crucible (ID 40 mm, 66 mm in depth), which was further protected by a graphite crucible. The weight ratio of slag/steel was added to 1:20 in order to make obvious difference. The reaction crucible was heated in a MoSi₂ furnace to 1873 K and held at that temperature for 20 minutes. The metal bath was stirred to promote reaction process once every five minutes by a molybdenum rod after the temperature reached 1873 K, for a total of five times. The experiment was carried out under argon atmosphere at a constant flow rate of 2 L/min to maintain the same atmosphere. After 20 minutes of experiment at 1873 K, which was confirmed to be enough to reach equilibrium by preliminary experiments, the crucible was taken out and cooled with a graphite lid. Sulfur content in steel was analyzed using a Q8 Magellan Direct Reading Spectrometer, and sulfur content in slag was calculated through the mass balance.

2.2. Effect of Slag Composition on LS

The experimental results are shown in Figs. 2 and 3. As shown in Fig. 2, the sulphur partition ratio increased with increasing %CaO/%Al₂O₃ ratio in the slag. It is known that increasing %CaO/%Al₂O₃ ratio results in the increase of CaO activity and sulphide capacity in slag. However, it should be noted that excessive CaO in slag may result in high melting point of the slag and deteriorate the slag fluidity and subsequently have detrimental effect on desulphurization during industrialization production.

Figure 3 shows the effect of CaF₂ content on the sulphur partition at 1873 K. The sulphur partition increased dramatically with increasing the CaF₂ content in slag from 10% to 15% while no big change in sulphur partition was deter-

Table 2. Composition of experimental desulphurization slags.

<table>
<thead>
<tr>
<th>sample</th>
<th>Compositions (mass%)</th>
<th>%CaO/%Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57.0 38.0 5 1.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>58.5 36.5 5 1.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>59.8 35.2 5 1.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>61.1 33.9 5 1.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>53.5 31.5 5 10 1.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>50.4 29.6 5 15 1.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>47.2 27.8 5 20 1.7</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of experimental setup for steel desulphurisation.

Fig. 2. Effect of (mass%CaO)/(mass%Al₂O₃) on sulphur partition.

Fig. 3. Effect of mass%CaF₂ on sulphur partition.
mined when the CaF₂ content in slag was further increased from 15% to 20%. As the desulphurisation progresses, CaS, the desulphurisation product of the reaction (1) is accumulated in the steel-slag interface preventing further desulphurisation, while the addition of CaF₂ can contribute to disintegration of the CaS layer formed at the interface and increase the dissolution of CaS in the slag.\(^{10-12}\) CaF₂ in the slag can also increase the amount of free oxygen ionic O \(2^-\) which is helpful in desulphurization reaction. Choi et al.\(^{13}\) pointed out that the sulfide capacity would increase with increasing CaF₂ content and finally become steady at CaO saturation. However, excessive CaF₂ content in slag is detrimental to desulphurisation because effective CaO concentration can be reduced. Furthermore, increasing the CaF₂ content in the slag may increase refractory corrosion and cause a number of environmental problems. Thus, the CaF₂ content in the slag should be reasonably controlled.

\[
\text{CaO} + \text{[S]} = (\text{CaS}) + \text{[O]} \hspace{1cm} (1)
\]

2.3. Selection of RH Desulphuriser

Based on the laboratory experiment results, the %CaO/%Al₂O₃ ratio of 1.8 is suitable for desulphurisation. However, this has to be further adjusted by considering the Al₂O₃ produced from Al deoxidation. The average oxygen content in steel before Al deoxidation in RH is 0.04%. The desulphuriser/steel ratio is 0.5%. Assuming the Al₂O₃ produced by Al deoxidation floats up completely into slag, the %CaO/%Al₂O₃ ratio must be about 3.5 in order to achieve the optimized %CaO/%Al₂O₃ ratio of 1.8. Therefore, the actual %CaO%/Al₂O₃ ratio in the desulphuriser is from 2.5 to 4.0 depending on the amount of deoxidiser added. The desulphuriser is produced by a pre-melting process. This pre-melting process restricts the CaF₂ content in the desulphuriser to be no more than 10% although the optimised CaF₂ content is 15%. Fluorspar was mixed with the pre-melted slag to increase the CaF₂ content to 15%.

The final desulphuriser is selected as mass%CaO/mass%Al₂O₃=2.5–4.0, CaF₂ < 15% and SiO₂ < 5% with melting point of below 1350°C. It is prepared by mixing pre-melted slag with additional lime and fluorspar. The particle size of desulphuriser is 3–5 mm. The particles finer than 3 mm were screened away by vacuum pump and while the coarser particles (bigger than 5 mm) were also removed as they slowed down the slag melting.

3. Thermodynamic Analysis of Top-slag

3.1. Relation between FeO Content and Oxygen Activity in Steel

Since the ultra-low-carbon electric steel was only lightly deoxidised by adding ferromanganese alloys during tapping, the FeO+MnO content in top slag is high which affects the oxygen activity in the steel. The oxygen activity in steel can be calculated from Reaction (2) to Eq. (4), if the activity of FeO in the slag can be obtained. Ohta et al.\(^{14}\) proposed a regression equation to calculate the FeO activity in CaO–SiO₂–Al₂O₃–MgO–(FeO+MnO) pseudo-quinary slag system; however, it is not suitable for the slag with high FeO content as in the current study. In the present study the FeO activity in slag is calculated using the thermodynamic package FACTSAGE.\(^{15}\) and subsequently the oxygen activity in the steel is calculated using Eq. (4) and the calculated FeO activity. Pure liquid FeO is taken as the standard state of FeO in slag. It should be pointed out that MnO is considered as FeO for the CaO–SiO₂–Al₂O₃–MgO–(FeO+MnO) pseudo-quinary slag system in this calculation, because they are both indicators of the oxidbillity of slag.

\[
(\text{FeO}) = [\text{Fe}] + [\text{O}] \hspace{1cm} (2)
\]

\[
\lg K = -\frac{6150}{T} + 2.60 \hspace{1cm} (3)
\]

\[
\lg a_{\text{FeO}} = \frac{6150}{T} + 2.60 \hspace{1cm} (4)
\]

The calculated oxygen activity in the steel is shown in Fig. 4 in comparison with the data measured by a Heraeus Multi-lab Celox Oxygen Determinator. It can be seen that the change tendency of the calculated oxygen activity reasonably agrees with the measured, but the calculated values are not seemed to agree with measured one for some heats. The possible reason is that steel melt was unstable and did not reach the equilibrium when oxygen activity was measured. The oxygen activity in the steel as a function of FeO+MnO content is shown in Fig. 5 when other components were defined as the average values of mass%CaO/mass%Al₂O₃=2.5, 9% SiO₂ and 10% MgO. The calculated values are in good agreement with the measured ones. The above results

\[\text{Fig. 4. Comparison of the calculated a}[O] \text{ with measured one.}\]

\[\text{Fig. 5. Effect of mass%}(\text{FeO}+\text{MnO}) \text{ on activity of oxygen.}\]
indicate that the oxygen activity decreases greatly with decreasing the FeO+MnO content in the slag. In order to improve the sulphur partition and prevent resulphurisation, the top slag should be deoxidised to lower the oxygen activity in the steel prior to adding desulphuriser in the RH degasser.

3.2. Effect of Slag Composition on $L_S$

Several models have been developed to estimate the sulphide capacity of slag, such as optical basicity model,\textsuperscript{17,18} KTH model\textsuperscript{19–21} and Pelton model (FACTSAGE thermodynamic package).\textsuperscript{22–24} By assuming the equilibrium of reaction (5) between slag and gas, the sulphide capacity of slag can be further calculated using Eq. (12).

$$1/2S_2+ (O^2-) = 1/2O_2+ (S^2-) .................. (5)$$

$$\log K^\Theta = -\frac{5.072}{T} + 0.293 ............... (6)$$

$$C_S = w(S) \times \left( \frac{P_{O_2}}{P_{S_2}} \right)^{1/2} = K^\Theta \times \frac{a_{O^2-}}{\gamma_{S^2-}} ............. (7)$$

Where $C_S$ is sulphide capacity of slag equilibrated with gas, $w(S)$ is the weight percentage of sulphur in the slag, $P_{O_2}$ and $P_{S_2}$ are the partial pressure of oxygen and sulphur in the desulphurisation reaction; $K^\Theta$ is the equilibrium constant; $a_{O^2-}$ is the oxygen activity in the slag; and $\gamma_{S^2-}$ is the activity coefficient of sulphur in the slag. The sulphide capacity of slag in equilibrium with steel can be further calculated using Eq. (9). The sulphur partition between slag and metal ($L_S$) can be obtained by Eq. (12).

$$[S]^+ [O^2-] = [O] + (S^2-) ....................... (8)$$

$$C'_S = w(S) \times \frac{a_{O^2-}}{a_{[S]^+}} = K^\Theta \times \frac{a_{O^2-}}{\gamma_{S^2-}} = K^\Theta \gamma_{S^2-} C_S .......... (9)$$

$$[S]+1/2O_2=[O]+1/2S_2..................... (10)$$

$$\log K^\Theta = -935/T + 1.375 ............... (11)$$

$$L_S = \frac{w(S)}{w[S]} = K^\Theta \times \frac{a_{O^2-}}{a_{[S]^+}} \times \frac{f_S}{a_{O^2-}} = C'_S \times \frac{f_S}{a_{O^2-}} ....... (12)$$

Where $C_S$ is the sulphide capacity of slag equilibrated with steel, $a_{[S]^+}$ and $a_{[S]^+}$ are the activities of oxygen and sulphur in steel, $w[S]$ is the weight percentage of sulphur in the steel and $K^\Theta$ is the equilibrium constant, and $f_S$ is the activity coefficient of sulphur in the steel.

Equation (12) indicates that for a given sulphide capacity, the sulphur partition between slag and steel is mainly dependent upon the activity coefficient of sulphur and the oxygen activity in the steel. Under the conditions of the current study, that is, both carbon and sulphur contents in the ultra-low-carbon steel are very low, and the activity coefficient of sulphur can be considered as unit. The oxygen activity in steel has already been calculated by Eq. (4). Thus the sulphur partition $L_S$ can be calculated by Eqs. (9) and (12).

Under current production conditions, the average sulphur content in steel before RH treatment is 0.006%, and the sulphur content in slag is 0.05%, which results in the sulphur partition ratio $L_S$ of about 8. In order to prevent resulphurisation, the sulphur partition should be more than 8 before RH treatment. After RH treatment, the decrease of sulphur content in steel and the increase of sulphur content in slag results in a further increase in the actual value of sulphur partition ratio; therefore the theoretical sulphur partition as calculated from Eq. (12) should be controlled much higher than 8.

The top slag for producing ultra-low-carbon electric steel was found to fall into following composition range: mass%CaO/mass%Al$_2$O$_3$=1–4, FeO=5–25%, SiO$_2$=6–12%, MgO=7–13% with the average value of %CaO/%Al$_2$O$_3$=2.5, FeO=15%, SiO$_2$=9%, MgO=10%. The effect of each component in top slag on $L_S$ was analysed by assuming the other components at their average values. The results are shown in Figs. 6 to 9.

As shown in Fig. 6(a), the sulphur partition $L_S$ decreases dramatically with increase in the FeO content in slag up to 15% whereas further increasing FeO content decreases the sulphur partition only marginally. The effect of FeO content in slag on sulphide capacity and FeO activity is shown in Fig. 6(b). It can be seen from Fig. 6(b) that the minimum of sulphide capacity of the slag against FeO content is around 15% FeO. The dramatically decreasing sulphur partition with increasing FeO content up to 15% is attributed to the decreasing of sulphide capacity and the increasing of FeO activity. Further increasing FeO content to above 15% increases both FeO activity and sulphide capacity, which result in a slowly decreasing sulphur partition.

In the production of ultra-low-carbon steel grades, both FeO and MnO have similar characteristics, and the FeO+MnO content should be controlled to less than 15% as shown in Fig. 6. Especially in the process of desulphurisation in RH degasser, the FeO+MnO should be controlled even lower to obtain higher $L_S$. 

![Fig. 6. Effect of mass%FeO on $L_S$, Cs and FeO activity.](image-url)
As shown in Fig. 7, increasing $\%\text{CaO}/\%\text{Al}_2\text{O}_3$ ratio (especially above 2.5) increases the sulphur partition between slag and steel, which is resulted from the decrease of FeO activity and the increase of sulphide capacity. Increasing $\%\text{CaO}/\%\text{Al}_2\text{O}_3$ results in the increase of free oxygen ionic $O_2^-$, and subsequently the increase of sulphide capacity as indicated by Eq. (5). On the other hand, the decrease of FeO activity is caused by the formation of the compounds between FeO and CaO resulting from the increased CaO content due to the increasing of $\%\text{CaO}/\%\text{Al}_2\text{O}_3$. The actual $\%\text{CaO}/\%\text{Al}_2\text{O}_3$ ratio should be controlled in the range of 2.5 to 4.0.

The effect of MgO content in top slag on $L_s$ is shown in Fig. 8. The sulphur partition increases slightly with increasing MgO content in the top slag from 7 to 13%, which can be explained by the slow decrease of FeO activity and the slow increase of sulphide capacity with MgO content. Similar trend has also been reported by Y. Taniguchi.\textsuperscript{25} It is well known that certain amount of MgO content in the slag benefits the life of the ladle linings while excessive MgO results in the high melting point and viscosity of the slag. Thus the actual MgO content in the slag is controlled at about 5%–8%.

Figure 9 shows the effect of SiO$_2$ on $L_s$. SiO$_2$ can decrease the sulphide capacity of the slag because oxide ions in the slag may decrease while the addition of SiO$_2$ increases the activity of FeO in slag. With the increase of SiO$_2$ content in the slag, part of CaO combined with FeO may be separated and integrate with SiO$_2$ so that the free
FeO content in slag increases. S. Bash et al.\textsuperscript{26} also reported that the activity coefficient of FeO increases with the increase of SiO\textsubscript{2}.

4. Industrial Trials

Industrial trials were carried out by controlling the oxygen potential (FeO+MnO content) via slag modification and adding RH desulphuriser investigated in this study. The (FeO+MnO) content and sulphur content in the slag, and the sulphur level in steel were analysed in samples obtained from vessel tapping to end product stage and were compared with the performance before industrial trial. The effect of slag FeO+MnO content on sulphur partition ratio and desulphurisation ratio was also calculated for various work stations. The RH desulphuriser compositions are shown in Table 3 according the chapter 2.3.

Figure 10 shows the effect of FeO+MnO content in slag on sulphur partition obtained from industrial trials (“after modification”) as well as the heats before industrial trials (“before modification”). The results clearly showed that the sulphur partition increased significantly with decreasing the FeO+MnO content in the slag when it was less than 15%. When the FeO+MnO content was higher than 15%, the sulphur partition was only about 5 and the effect of FeO+MnO on LS was small. This indicates the importance of controlling the FeO+MnO content in slag to prevent resulphurisation. The results from industrial trials were in good agreement with the thermodynamic prediction as shown in Fig. 6.

Figure 11 shows the effect of %CaO/%Al\textsubscript{2}O\textsubscript{3} on sulphur partition. The industrial results are also in good agreement with thermodynamic calculation as shown in Fig. 7, i.e. the sulphur partition increased with increasing %CaO/%Al\textsubscript{2}O\textsubscript{3} in the slag.

The change in the sulphur level of the steel at different working stations was shown in Fig. 12 for the periods of both industrial trials (30 heats) and before industrial trials (18 heats). Figure 13 shows the desulphurisation ratio ($\eta_S$, mass%) at the points of before RH and RH refining in the periods of both industrial trials and before industrial trials. By controlling the FeO+MnO content in the slag via slag modification and by adding RH desulphuriser, the average desulphurisation ratio was up to 34.1% with a maximum of 61.7% after LF and RH process, in comparison with resulphurisation of –2.0% in average with maximum 16.7% during the period of before industrial trials.

After controlling the oxygen potential in the slag and adding RH desulphuriser in RH degasser, the average steel sul-

<table>
<thead>
<tr>
<th>%CaO/%Al\textsubscript{2}O\textsubscript{3} compositions (mass%)</th>
<th>SiO\textsubscript{2}</th>
<th>MgO</th>
<th>F\textsuperscript{−}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5–4</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;8</td>
</tr>
</tbody>
</table>

Fig. 10. Effect of mass% (FeO+MnO) in slag on sulphur partition $L_S$.

Fig. 11. Effect of (mass%CaO/ mass%Al\textsubscript{2}O\textsubscript{3}) content on $L_S$ (All data are from the heats before slag modification).

Fig. 12. Comparison of sulphur content at different work stations before and in the industrial trials.
phur level after RH treatment was 0.0043% and the sulphur level in end product was less than 0.005%, which meets the requirement of ultra-low-carbon electrical steels. The results from the industrial trials proved that by modifying the top slag and by adding desulphuriser in RH degasser ultra-low-carbon electrical steels can be successfully produced in the steel plant.

5. Conclusions

(1) For RH desulphurisation, a CaO–Al2O3–CaF2–based desulphuriser was developed by laboratory desulphurization experiments and by considering the floating of deoxidation products (Al2O3). The optimised composition of the RH desulphuriser is mass%CaO/mass%Al2O3=2.5–4; SiO2<5% and F <8% with the melting point of below 1350°C.

(2) Effect of top slag composition on sulphur partition between slag and steel was analysed using thermodynamic package FACTSAGE. It was found that FeO+MnO content in the top slag should be controlled lower than 15% before RH treatment and below 10% after RH treatment. The sulphur partition increases with increasing %CaO/%Al2O3 and decreasing SiO2 content in the top slag, but the effect of MgO content on Ls is small.

(3) Industrial trials were carried out by controlling the FeO+MnO content in the top slag via slag modification and adding RH desulphuriser. The FeO content in the slag was controlled to lower than 15% before RH treatment and to lower than 10% after RH treatment. Resulphurisation was effectively prevented and the average desulphurisation rate in RH degasser was up to 34.1%.

(4) By modifying the top slag and by adding desulphuriser in RH degasser ultra-low-carbon electrical steels with sulphur content less than 0.005% can be successfully produced via soft-killed BOF-LF-RH-CC process route.

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