Keywords: High strength steel, Pickling model, Derivative near zero.

Abstract. The effects of acid concentration, temperature and the thickness of strip oxide scale on the pickling time of high strength steel were studied and a pickling time mode was established. The end time of acid pickling was determined by introducing the electropotetial derivative near zero method. The effects of different pickling temperatures and acid concentrations on the pickling time of different thickness scales were studied by further experiments. When increase acid concentration to 10%, pickling time is greatly reduced, and continue to increase the acid concentration will have little help to shorten the pickling time. When the acid temperature reaches 80℃, the pickling efficiency reaches the highest value. If the temperature continuous to increase, it will not only waste energy but also increases the volatilization of hydrochloric acid. The comprehensive pickling model was established and the actual high strength steel pickling data was brought into the test. The proposed comprehensive pickling model in this paper has better accuracy and validity than the old ones.

Introduction

With the continuous development of the automobile manufacturing industry, the demand for the product quality has been improved. High strength steel [1,2] is widely used because of its light weight and high strength. However, the surface quality problems in the production process of high strength steel have been restricting its further development. High strength steel was rolled and coiled in high temperature [3]. Oxide scale is firmly covered on the strip surface, which will have a negative impact on the subsequent cold rolling product if not be descaled. So before cold rolling the pickling method will be used to remove oxide scale. In order to ensure the high strength steel pickling effect, numerous factors need to be considered such as materials of different finishing temperature and coiling temperature, straightening and pickling process parameters. In order to determine the end time of pickling accurately, a developed method based on the initial potential derivative zero method proposed by Shu-jie Chen[4,5] et al, was used in this article.

At present, experts from domestic and foreign had conducted much work on pickling model. Liu Jiang [6] hold opinions that the acid temperature is a function of the best strip speed, and the acid liquid turbulence is also the function of acid temperature. Hudson[7-9]had studied the effects of acid concentration, temperature and speed of the strip on acid pickling time, and think that when the acid temperature is low, elongation rate for pickling promotion effect is obvious. But when the temperature is high, the effect of elongation rate to enhance the speed of picking is weak. Gaines[10] ,on the basis of the Hudson formula, introduced the effect of the concentration of ferrous ions on the pickling time. Zi-liang Yang [11] considered the effect of the process parameters on the pickling, and obtained the formula of the pickling time model under the condition of tension and compression. Su-juan Shao [12,13], on the basis of Zi-liang Yang, found that the amount of pressure during descaling process is the decisive factor, therefore she ignored the factors of tension, and added the influence of turbulence of acid in mathematical model. Above models have considered many factors including acid pickling temperature, concentration, turbulence, straightening process parameters on the pickling time. But all of these are external factors in the pickling process, and do not contain any characteristics of oxide, such as oxide thickness. For high...
strength steel, the thickness of the oxide sheet is very sensitive to the temperature during the hot strip rolling process [14,15]. So in the hot strip continuous pickling line, the thickness of oxide scale of hot rolled high strength steel must have an important effect on the pickling time. Therefore, it is necessary to take into account the influence of strip thickness on the pickling time to improve the production efficiency and product surface quality.

**Acid Electropotential Derivative Near Zero Method**

A series of oxidation-reduction reactions will occur on the surface of the steel strip during the pickling process. The acid firstly react with outer scale, then penetrate into the oxide slit, and react with inner oxide scale which is easier to solute in acid. With the dissolution of the inner scale, matrix gradually began to contact with acid. In this process, the potential changes constantly, but will be stable in a certain potential value in the end (The stable potential of the reaction between acid and matrix), which means the end of pickling. The basic device of the pickling experiment is shown in figure 1.

![Schematic diagram of pickling test device.](image)

Hot rolled strip sample of high strength steel was put in hydrochloric acid solution with temperature of 80°C and concentration of 12% in the pickling experiment. In theory, at the end of the pickling, the potential will not change, and the derivative value of the potential curve is zero, and does not change with the increase of time. However, in practice, the change of electric potential is very complicated. At the end of the pickling, The potential curve cannot really show the horizontal line or unchanged, but because of the high iron surface residues and other factors lead to curve tends to level slowly, the derivative curve for a long time are not equal to 0. While the longtime of acid picking will consume the iron matrix, resulting in excessive pickling. Therefore, how to quickly and effectively determine the end time of pickling is very important to the efficiency and quality of pickling.

Our previous research results showed that the pickling time potential derivative of high strength steel is not equal to zero for a long time. According to the experimental results, we found that when the electric potential derivative reaches -0.0025V/s, the acid pickling is over, and continuous pickling will only waste time and energy, which leads to the phenomenon of excessive pickling finally. The method of determining the end time of the picking was called as electropotential derivative near zero method.

**Study on Influencing Factors of Strip Pickling**

**Effect of Different Acid Concentration on Acid Pickling Time of Different Thickness of Oxide Scale**

According to the electropotential derivative near zero method, the variation of pickling end time for
different high strength steel samples changed with oxide thickness ($\delta$) and hydrochloric acid concentration under different pickling temperature (75°C, 80°C and 85°C) as shown in figure 2-figure 4.

Figure 2. The effect of different acid concentration on the acid pickling time of the five kinds of steel strips at the temperature of 75°C.

Figure 3. The effect of different acid concentration on the acid pickling time of the five kinds of steel strips at the temperature of 80°C.
Figure 4. The effect of different acid concentration on the acid pickling time of the five kinds of steel strips at the temperature of 85°C.

It can be seen from the figures, with the increase of hydrochloric acid concentration, the time of pickling is decreased, and it has the same rule for five kinds of oxide scales. Under the same temperature condition, the concentration of the acid increased significantly from 5% to 10%, and the pickling time decreased slowly when the concentration increased from 10% to 12%. When the acid concentration is over 10%, the effect is not obvious.

Effect of Temperature Change of Acid Solution on the Acid Picking Time of Different Thickness Oxide Scale

Under the condition that the acid concentration (5%, 10%, 12%) remains unchanged, the pickling time curve varied with the different oxide thickness ($\delta$) in hydrochloric acid of different temperatures, which are shown in figure 5- figure 7.

Figure 5. The effect of different acid temperature on the acid pickling time of five kinds of steel strip with the concentration of acid was 5%. 
It can be seen from above figures, with the increase of temperature of hydrochloric acid, the time of acid pickling is decreased, and it has the same rule for five kinds of oxide scales. Under the condition of the same concentration, when the temperature is increased from 75°C to 80°C, the acid picking time obviously decreased, and when the temperature is increased from the temperature of 80 °C to 85 °C, the pickling time decreased slowly. Continue to improve the temperature of the acid, it will not only increase energy consumption, but also has less help for shortening the time of pickling.

**Establishment of Comprehensive model of Acid Temperature, Concentration and Oxide Thickness**

Based on the above experimental data, the relationship between the picking time and the acid concentration and the thickness of oxide scale was studied at the temperature of 75 °C. The thickness parameter ($\delta$) is used to fit the five sets of data again, and the expression of $t$ is obtained:

$$t = -0.00215C\delta - 1.14907C + 0.7144\delta + 34.516$$  \hspace{1cm} (1)$$

Similarly, the curve of pickling time, acid concentration and oxide thickness is established by curve fitting, which is shown in the formula (2) and formula (3) when the temperature is 80°C and 85°C.
\[ t = -0.0014C - 1.9032C + 0.7239\delta + 29.575 \]  
\[ t = -0.00283C - 1.19032C + 0.7239\delta + 27.858 \]

Based on the comprehensive analysis of the above curves and formulas, the comprehensive model of acid pickling time (t) with acid temperature (T), concentration (C), and oxide thickness (\delta) were obtained, as shown in formula (4).

\[ t = 12.306C + 0.32\delta - 0.67T - 0.275C\delta - 0.34CT + 0.0052\delta T + 0.007C\delta T \]

\[ -4.36 \times 10^{-5}C\delta T^2 + 0.00214CT^2 + 83.915 \]  

The experimental data of this model are verified by the test data selected randomly, and the results are shown in table 1.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Thickness (mm)</th>
<th>Temperature T(°C)</th>
<th>Measured value(s)</th>
<th>Calculated value(s)</th>
<th>Error(%)</th>
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<tbody>
<tr>
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<td>34</td>
<td>36</td>
<td>5.8</td>
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<tr>
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<td>80</td>
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</table>

The results show that the error between the model acquisition time and the actual acid pickling time is less than 8%.

**Conclusion**

1. Under the same temperature condition, when the concentration increased from 5% to 10%, the acid pickling time decreased obviously, and when the acid concentration increased from 10% to 12%, the time decreased slowly. Continuing to improve the concentration of hydrochloric acid, it will not only increase the volatilization of hydrochloric acid, but also have little help to shortening the pickling time. On the other hand, under the same concentration condition, when increased the acid temperature from 75°C to 80°C, the time of acid pickling obviously decreased, and when the temperature is increased from the temperature of 80°C to 85°C, the pickling time decreased slowly.

2. In this paper, a comprehensive mathematical model of acid pickling time, acid temperature, concentration and oxide thickness of high strength steel was established, through the test, we find that the time error can be less than 8%, which has high accuracy and effectiveness.

**Acknowledgement**

This research was financially supported by the Natural Science Foundation of China (51105143, 51675182).

**References**


