

## Pickling Kinetics of Tertiary Oxide Scale Formed on Hot-Rolled Steel Strip

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### Abstract

During hot rolling process a steel strip covers with oxide scales. These scales have to be removed by acid pickling process. This work focuses on the study of the scale removing rate of a hot-rolled steel strip in order to find an expression explaining the rate of reaction in hydrochloric acid. The study of scale removal is accomplished by utilizing the pickling simulator with different acid concentrations and pickling temperatures.

There are two approaches that can be used to find a scale removing rate; the measurement of weight change and the iron concentration change after the pickling process. In this work, the measurement of the change of iron concentration was selected because it represents the actual amount of the scale removed after the pickling process. The experimental data were used to derive the expression for the rate constants. By using these expressions, the pickling equations can be obtained. These equations are capable of predicting the maximum removable scale thickness during the pickling process for several pickling conditions; i.e. time needed for scale removal.

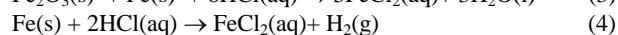
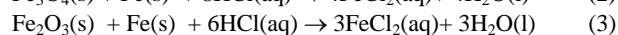
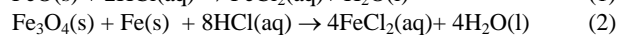
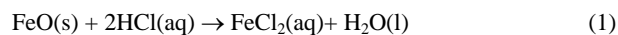
**Key words:** Oxide scale, Hot-rolled steel strip, Scale dissolution rate

### Introduction

After the hot rolling process, oxide scales are formed on the surface of a steel strip. These scales affect the following processes such as cold rolling, forming etc. Scale removing is the essential process that increases the value of steel strip products. The most popular approach is the continuous acid pickling in which the steel strip is immersed in a series of acid tanks with different concentrations.<sup>(9)</sup> Acid with the lowest concentration is generally placed in the initial tank, and the highest concentration is placed in the final tank. Hydrochloric acid is widely used because it requires less pickling time and yields uniform surface finish. The scale structures may vary depending on processing parameters, such as the finishing and coiling temperatures, the cooling rate, and the environment in which steel strips are coiled. The oxide scales usually have different types of iron oxide and thickness at each location of the strip coils.<sup>(1)</sup> These differences result in a non-uniform

scale dissolution rate along the strip. The descaling rate is a very important factor which does not only define the efficiency, but also the conditions, of the pickling process.<sup>(2-4)</sup>

The chemical reactions involved in pickling revealed that iron oxides and metallic iron react with hydrochloric acid; then ferrous chloride, water, and hydrogen gas are formed.



The reaction in equation (4) can be prohibited by inhibitors which minimize the loss of base metal and lower the acid consumption for pickling.

Many studies showed the relationship between scale structures and picklability, but the rate of oxide dissolution has not yet been identified.<sup>(3-6)</sup>

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Most of them reported that the scale which is comprised of hematite is hard to be pickled. These facts coincide with the problems occurred in the factory. Strip coils are pickled in a non-uniform way, consequently leaving the scale at the coil edge. This paper focuses on finding the proper equation which can be used to predict the pickling process of the edge's scale.

## Materials and Experimental Procedures

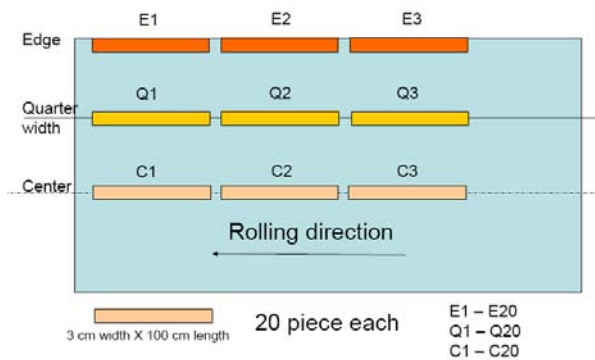
### Materials

The samples used in this study are taken from Sahaviriya Steel Industries Public Co., Ltd. The hot-rolled steel strip HR1 grade is processed with finishing temperatures varying from 845°C to 905°C and coiling temperatures are in the range of 545-625°C. The steel composition is given in Table 1.

**Table 1.** Chemical composition (wt.%). Hot-rolled steel strip, 3.2 mm thickness.

C	Si	S	P	Mn	Ni	Cr	Mo
0.06	0.02	0.01	0.01	0.25	0.055	0.008	0.005
V	Cu	Ti	As	Sn	Al	B	Nb
0	0.026	0.003	0	0	0.032	0.0002	0

Along the width of the strip, the samples are cut from the edge (sample E), quarter width (sample Q) and center (sample C) of the head of the strip coil. Each sample is cut into small coupons, sized 3×5 cm. The locations of these samples are shown in Figure 1.



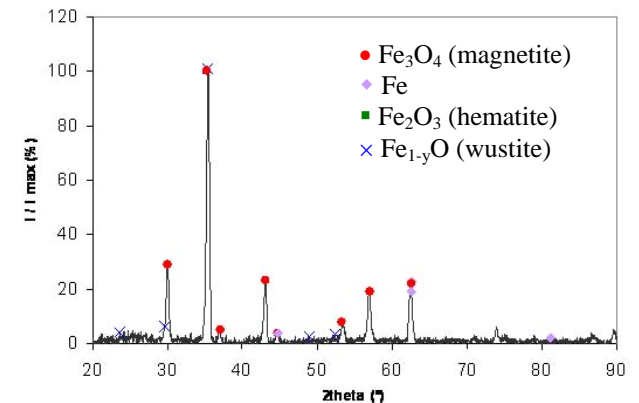
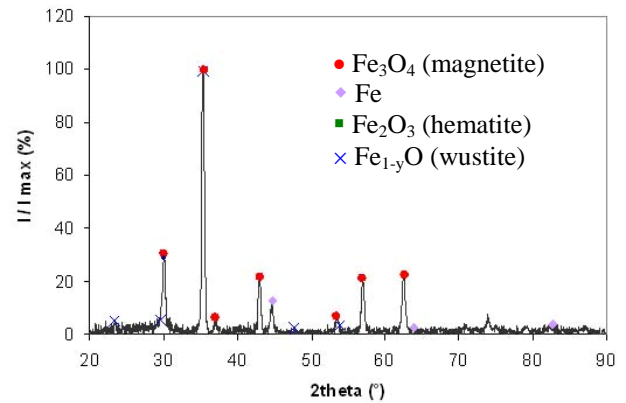
**Figure 1.** Specimens used for pickling test.

### Scale Characterization

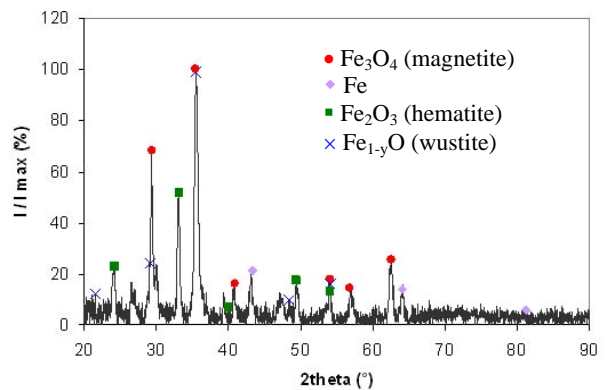
Tertiary oxide scale occurred before and after finishing the rolling process can be divided into 3 types according to their composition. There are wustite(FeO), magnetite(Fe<sub>3</sub>O<sub>4</sub>), and hematite(Fe<sub>2</sub>O<sub>3</sub>).

Scale composition is determined by X-ray diffraction (XRD). The scales found at the quarter width and center of coil are mainly magnetite, Figure 2. At the edge location, the scales are found to be magnetite and hematite, Figure 3.

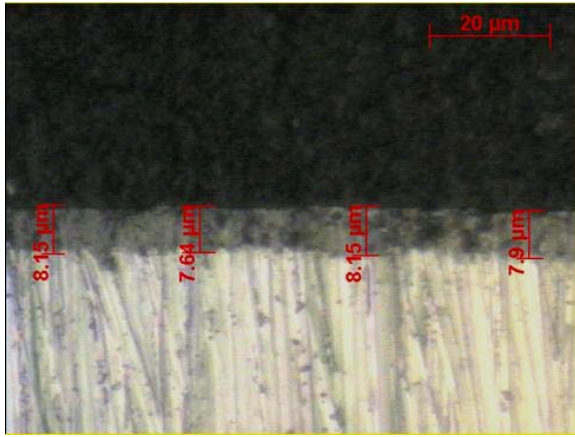
The scale thickness of coupons is determined by cross-section measurement, Figure 4. The total scale thickness at the edge location coupon is larger than of scales at the center and quarter ones, with an average thickness of 9.62, 7.88 and 6.63 μm, respectively.



**Figure 2.** XRD results for scales found at the center (left) and quarter width (right).



**Figure 3.** XRD result for scales found at the edge.



**Figure 4.** Cross-section of the scales at the center of the coil.

### Pickling Test

Laboratory scale pickling tests are adapted from a 4-tank pickling simulator. The set-up comprises of two beakers containing acid and rinsing solutions. The acid solution is prepared by diluting concentrated hydrochloric acid solution. This solution was renewed for each test to ensure that all tests are performed under the same conditions with no iron content. Specimen was held and dipped by using special grip made from acrylic.

For pickling test, the side edges of steel coupons are coated with a chemical resistance film, Epigen 4029FC, in order to prevent the dissolution of the steel at the edge surface. After cleaning the coupons with ethanol, they are dipped into the well-stirred hot acid bath (900 RPM) for 5, 10, 15, 20 and 30 seconds. Then they are rinsed in the rinsing bath and cleaned further by using running water and ethanol, respectively. The conditions are given in Table 2.

**Table 2.** Conditions for pickling test.

Temperature	70°C	80°C	90°C
Concentration (g HCl/l)	40	40	40
	70	70	70
	100	100	100
	130	130	130

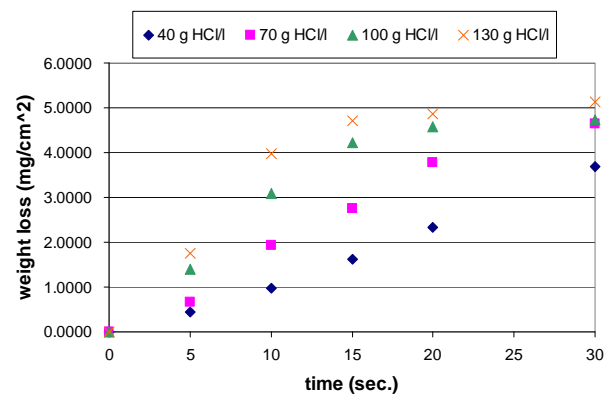
### Determination of the Pickling Rate

The pickling rate can be determined by two methods, the weight loss of steel coupons and the amount of iron content in acid solutions. The amount of scale removed by pickling is determined by measuring the weight change of coupons after the pickling test. The weight loss is expressed in  $\text{mg}/\text{cm}^2$ . The total iron content in solution, reported in ppm, is determined by Inductive Coupled Plasma (ICP) Perkin Elmer model PLASMA-1000.

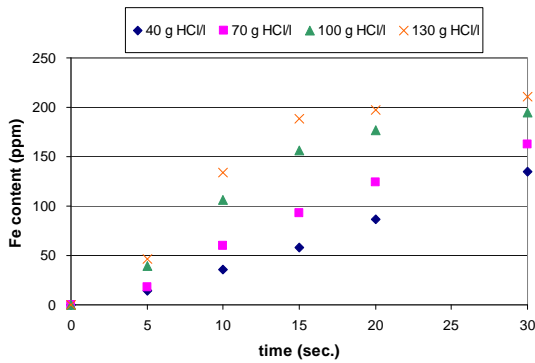
### Results and Discussion

While dipping the samples cut from the edge of the strip in hydrochloric acid, bubble gases are gently formed on their surface. These gases are the result of the reaction between decomposed Fe and hydrochloric acid solution. It is known that decomposed Fe is formed during the cooling of the coil;  $4\text{FeO}(\text{s}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) + \text{Fe}(\text{s})$ .<sup>(3-5)</sup> The longer the pickling time, the more bubble gases are formed. These gases appeared at preferred sites, which indicated that the outer scale layers are not dense. Therefore, the acid solution can penetrate into the scale layer and react with decomposed Fe particles underneath.<sup>(11)</sup> These bubble gases are hydrogen gas, as shown in equation (4). As the results illustrate, the scales are not dissolved layer by layer.

When most of the scales were removed and the base metal was revealed, the bubble gases generated all over the specimen surface can be observed, indicating the completion of the pickling process (as these gases came from the reaction between acid solution and base metal). It can be concluded that these porous scales cause a non-uniform pickled surface.



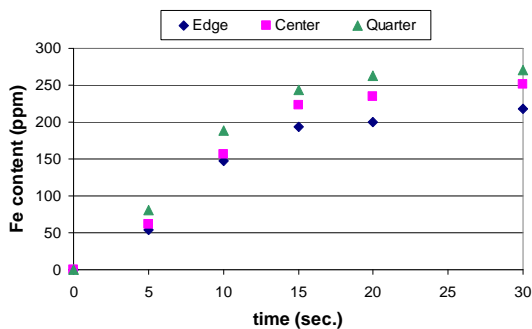
**Figure 5.** Weight losses after pickling at 80°C.



**Figure 6.** Fe content after pickling at 80°C.

Figure 5 shows that weight losses increase with increasing acid concentration and time. The result from Figure 6 also shows the same trend. However, after pickling test of all conditions, there are non-dissolved or very slowly dissolved scale particles which have fallen to the bottom of the pickling beakers. Therefore, specimen weight loss will not show the exact change of the system. Fe content measurement is chosen to represent the results of pickling test because it truly identifies the scale dissolution rate. Pickling in 40g HCl/l solution, iron content gradually increases in straight line for all temperatures. The others show rapid change in the first 15 seconds; afterwards, a slower change occurs after most scales are removed. These changes show that the reaction between acid and scales is much more rapid than the reaction between acid and iron base metal.

In comparison with the specimens taken from other locations of the strip coil, one taken from the edge location seems to be dissolvable in acid solution as shown in Figure 7 with most difficulty. Typically, the edge of the coil is exposed to the air longer than any other area. Therefore, not only magnetite, but also hematite is favored to form on this surface area, Figure 3. Especially at the head of coils, scales located at the edges are thickest. Scales at quarter width and center locations are found to be magnetite, which can be dissolved in acid solution more easily than the oxide structure found at the edges.<sup>(10)</sup>

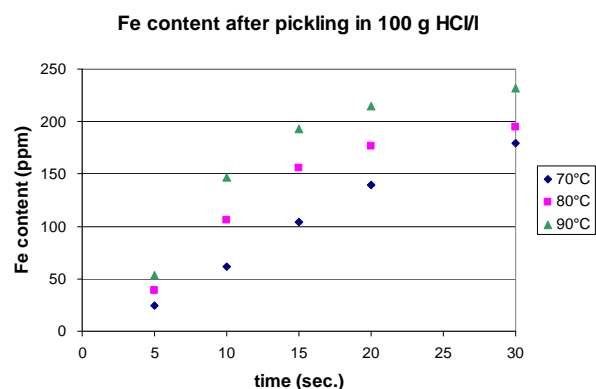


**Figure 7.** Fe content after pickling in 100 g HCl/l 90°C.

Figure 8 shows the temperature effect on the dissolution of oxide scales in HCl solution in the form of Fe content. As expected, it is clearly shown that the higher the temperature is the faster the dissolution rate is obtained. By using experimental results conducted under several temperatures and several acid concentrations, one can theoretically construct expressions which relate time and oxide dissolution. However, due to the fact that scales at different locations are composed of different ratio of scale types (hematite to magnetite and wustite), and each type of scale dissolves at a different rate. It is not possible to construct such expressions using data from this work to include the effect of each scale type ratio. To simplify the situation, in order to get rather practical expressions for predicting the pickling process, several assumptions as the following have been established:

1. The presence of hematite in the scale at the edge of the coil will be ignored and the complete scale is assumed to be magnetite.

2. Ignoring the presence of hematite does not significantly vary the overall scale dissolution rate. This is confirmed by the experimental observation that the red oxide scale did not form a dense layer on the surface, and during the pickling process it is removed from the surface by peeling out and falling down to the bottom of the pickling tank rather than dissolving. The underneath layer which is magnetite can be directly dissolved. Due to the fact that magnetite is the thickest scale layer, its dissolution reaction (equation (2)) can be assumed as the rate controlling step for the scale dissolution process, and it is used to derive expressions for the pickling prediction.

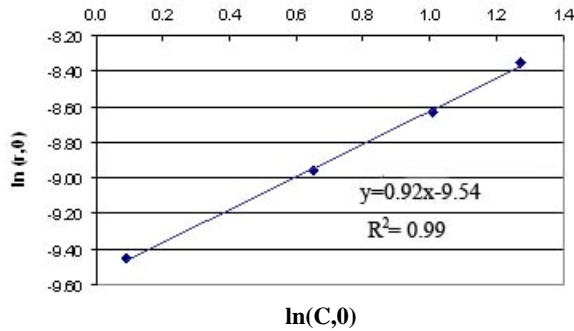


**Figure 8.** Fe content after pickling in various temperatures.

In order to construct expressions, the reaction order has first to be determined. Using equation (2), measured iron content is modified to hydrochloric change in the pickling tank. By using the differential analysis method, the reaction order (n) can be obtained.

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Plotting the relationship between acid concentrations and pickling time, the initial slopes which indicate the initial dissolution rates can be defined in the first five seconds of the pickling test. Subsequently, the relationship between these initial dissolution rates and the starting concentration of each condition is plotted. The slope of this curve will yield the reaction order as shown in Figure 9. They are 0.92, 1.09 and 0.97 for pickling at 70, 80 and 90°C, respectively.



**Figure 9.** Reaction order of pickling at 70°C.

The order is nearly 1 for all three temperatures. The rate law is shown as equation (5).

$$r_{\text{HCl}} = kC_{\text{HCl}} \quad (5)$$

Then

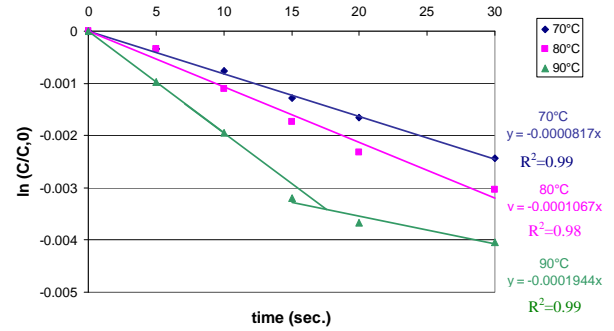
$$-\frac{dC_{\text{HCl}}}{dt} = kC_{\text{HCl}} \quad (6)$$

Integrate equation (6)

$$\ln \frac{C_{\text{HCl}}}{C_{\text{HCl},0}} = -kt \quad (7)$$

Plotting the relationship between time and concentration, equation (7), the rate constant ( $k$ ) can be found. The slopes of the curves in Figure 10 represent the reaction rate constant. Under some conditions, especially for the higher concentration and temperature, there are two different slopes which identify the change of main reaction in the pickling test. In this work, the initial slope of about the first 15 seconds is selected because it represents the main reaction between scales and acid solution. The latter slope is, instead, the rate constant for the reaction between the acid solution and iron base metal which seems to be much slower than the initial slope. The time interval for the initial slope is called initial period; for the latter slope it is called latter period. The connection between both periods indicates the time when the main reaction of system is changed. The rate constants of the

initial period are shown in Figure 10 and Table 3 for all conditions.

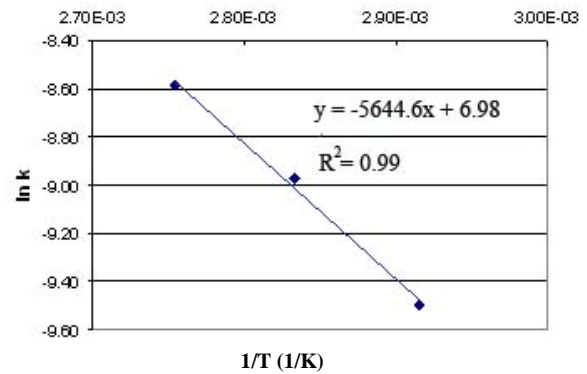


**Figure 10.** Hydrochloric acid concentration changes after pickling in 70 g HCl/l.

**Table 3.** Rate constant of each condition.

Starting hydrochloric acid concentration	Rate constant ( $s^{-1}$ )		
	Temp. 70°C	Temp. 80°C	Temp.90°C
40 g HCl/l (I)	$8.64 \times 10^{-5}$	$1.41 \times 10^{-4}$	$1.91 \times 10^{-4}$
70 g HCl/l (I)	$8.17 \times 10^{-5}$	$1.07 \times 10^{-4}$	$1.94 \times 10^{-4}$
70 g HCl/l (L)	-	-	$5.35 \times 10^{-5}$
100 g HCl/l (I)	$8.07 \times 10^{-5}$	$1.31 \times 10^{-4}$	$1.82 \times 10^{-4}$
100 g HCl/l (L)	-	$3.26 \times 10^{-5}$	$3.24 \times 10^{-5}$
130 g HCl/l (I)	$7.52 \times 10^{-5}$	$1.27 \times 10^{-4}$	$1.86 \times 10^{-4}$
130 g HCl/l (L)	$4.24 \times 10^{-5}$	$1.53 \times 10^{-5}$	$3.18 \times 10^{-5}$

(I): Initial period, (L): Latter period



**Figure 11.** Arrhenius plot of pickling in 130 g HCl/l.

The temperature effect on the scale dissolution rate can be expressed in the form of Arrhenius equation. It shows the relationship between temperature and rate constant. In order to obtain the equation, the plot between  $\ln k$  and  $1/T$  has been done as shown in Figure 11. The rate constants used in this plot are taken from the initial reaction period which identifies the rate of scale dissolution. The Arrhenius equation is

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

$$\ln k = \left(-\frac{E_a}{RT}\right) \cdot \frac{1}{T} + \ln A \quad (9)$$

The slope yields the activation energy ( $E_a$ ), and Y-intercept yields the pre-exponential factor or Arrhenius' constant ( $A$ ) which shows the possibility of atom collisions. The average activation energy of all conditions is 43,704 J/mol or 10.44 kcal/mol. Substituting equation (8) in (7) results in a pickling equation in the form of equation (10) as shown in Table 4.

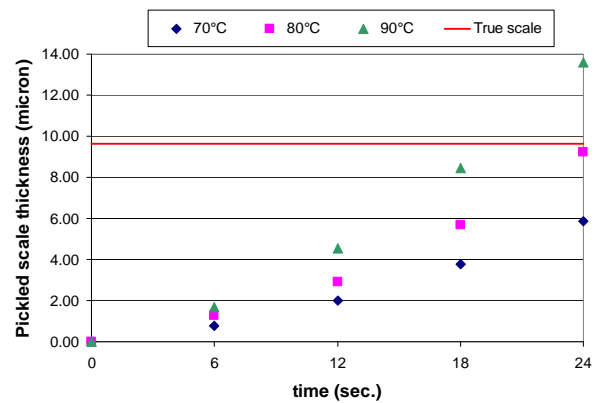
$$\ln\left(\frac{C_{\text{HCl}}}{C_{\text{HCl},0}}\right) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot t \quad (10)$$

**Table 4.** Pickling equations.

Hydrochloric acid concentration	Pickling equation
40 g HCl/l (1.096 mol/l)	$\ln\left(\frac{C_{\text{HCl}}}{1.096}\right) = -163.40 \cdot \exp\left(-\frac{41139}{RT}\right) \cdot t$
70 g HCl/l (1.918 mol/l)	$\ln\left(\frac{C_{\text{HCl}}}{1.918}\right) = -476.85 \cdot \exp\left(-\frac{44589}{RT}\right) \cdot t$
100 g HCl/l (2.740 mol/l)	$\ln\left(\frac{C_{\text{HCl}}}{2.740}\right) = -217.07 \cdot \exp\left(-\frac{42158}{RT}\right) \cdot t$
130 g HCl/l (3.562 mol/l)	$\ln\left(\frac{C_{\text{HCl}}}{3.562}\right) = -1075.03 \cdot \exp\left(-\frac{46929}{RT}\right) \cdot t$

A pickling equation is useful for predicting the results of pickling. Knowing conditions of pickling; i.e. temperature, concentration or time, the amount of pickled scale can be calculated or vice versa. The oxide scale formed at the edge of the strip in this study, for example, has an average thickness of 9.62  $\mu\text{m}$ . The pickling process is usually performed at the rate of 133-143 m/minute, the pickling time in each tank is about 6 seconds. When substituting the time in the pickling equation, the results of the pickled scale are in the form of hydrochloric acid concentration after pickling. Using the equation (2) can predict the amount of magnetite which exists in the scale. Then the approximate amount of magnetite can be converted into the scale thickness, assuming the density of magnetite is 5.18  $\text{g}/\text{cm}^3$ . Figure 12 shows the example of the pickling process prediction. The condition is defined as a continuous pickling process starting from 40, 70, 100 and 130g HCl/l, respectively. All concentrations are set to the same

temperature. The thickness of the pickled scale is defined for the three temperatures 70, 80, and 90°C. The results show that scales are completely removed when the pickling temperature is set at 90°C. It is known that the actual pickling process has no pre-heater tank and the first acid tank is usually set at a higher temperature than the others. This provides a reaction at nearly constant surface temperature in all tanks. In general the temperature of the first tank is usually not set at more than 90°C, and then the temperatures of the latter tanks are lessened. Thus, the amounts of actual pickled scale should be less than those predicted from the pickling equation. The prediction error may arise from the limitation of the experimental set up; i.e. the stirring rate of the acid solutions that is slower than the actual moving rate of the steel strip.



**Figure 12.** Prediction of pickling process by using pickling equation.

## Conclusions

This work investigates the effect of pickling temperature and hydrochloric acid concentrations on the rate of oxide scale dissolution. The scale removing rate increases with increasing temperature and/or concentration. Due to the excessive amount of oxygen, the scale formed at the edge is the thickest and composed of both magnetite and hematite. This is also found in a previous study conducted by Chen, *et al.* (2000-2003) and Kizu, *et al.* (2001)

The scale dissolution rate can be divided into two periods. The initial period, as the principal reaction, is the reaction between acid solution and scale which yields a very high rate. The latter period is the rate constant for the reaction between acid solution and iron base metal which can be indicated when the bubble gases are generated from the entire surface of the specimen.

In this work, the effect of pickling acid concentration and temperature on the rate of scale removing were studied. The experimental data were used to derive the rate constant and activation energy, and finally the pickling equations were obtained. Considering the fact that the actual pickling process and scale structure are very complicated, all the equations above are derived based on different assumptions. To some extent, they are surprisingly still capable of predicting the thickness of removable scales during the pickling process for several actual pickling conditions.

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