Rapid and Continuous Analysis Method for Steel Pickling Solution Using Near-Infrared Spectroscopy†

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Abstract:

As a rapid analysis method for the pickling solution in steel production lines, near-infrared spectroscopy (NIR) was applied to measure the concentrations of acid and iron in acid pickling solutions. The results of experiments revealed that the concentrations of acid and iron can be calculated by multivariate analysis by using the measured spectra of solutions containing varied amounts of acid and iron ions. An actual pickling line test was performed, and a good correlation between the NIR results and the chemical analysis values was obtained. It was also found that long-term continuous measurement is possible by utilizing this system.

1. Introduction

In steel-making processes, an oxide layer called scale forms by heat treatment on the surface of steel sheets. Scale must be removed by pickling, as it has an adverse effect on the appearance and properties of steel products. However, over-pickling causes roughening of the surface layer of the steel sheet and shortens the life of the pickling solution. For these reasons, control of the acid concentration in the pickling process is extremely important for securing stable product quality. Moreover, because changes in the concentration of the pickling solution per unit of time have also tended to increase as a result of the higher line speeds of recent years, faster control of the pickling solution concentration than in the past is now considered necessary[1,2].

The control items for pickling solutions are acid concentration and metal ion concentration. Widely used measurement methods include the neutralization titration method for measurement of the acid concentration, and atomic absorption spectrophotometry (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), etc. for analysis of metal ions[3]. However, the titration method is complicated and takes long measurement time, and it is necessary to prepare reagents and treat the waste solution. Although AAS and ICP-AES offer fast response, there are restrictions on installation locations, and these methods are not suitable for *in-situ* analysis in steel-making processes. As an additional problem, it is necessary to use a combination of these techniques in order to analyze both the acid and metal ions.

In recent years, near-infrared spectroscopy (NIR) has been applied as an acid concentration control method for product washing solutions and etchants in semiconductor and electronic device production processes[4–6]. NIR has attracted attention as a suitable technique for rapid on-line or on-site measurement, as it offers a short measurement time and excellent maintainability and also does not require chemical solutions. However, in spite of these advantages, there were no reported examples of application of NIR in the steel industry. Therefore, in order to realize high speed and reduce the burden of pickling solution analysis in steel-making processes, the authors carried out a study of continuous concentration measurement of pickling solutions in steel-making processes by using NIR. The results are reported in the following.

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2. Experimental

2.1 Apparatus and Sample Materials

The schematic diagram of the apparatus used in this research and the measurement conditions are shown in **Fig. 1** and **Table 1**, respectively. The analysis apparatus was a near-infrared spectrometer, NR800, manufactured by Yokogawa Electric Corporation. Incident light is introduced into the measurement cell by an optical fiber, and the transmitted light is detected by a photodetector. The absorption spectrum is obtained by taking Fourier transform.

The conditions of the solutions used in the study are shown in **Table 2**. In this research, 10 samples each of simulated pickling acid solutions and actual pickling acid solutions were used. The simulated solutions were prepared by dissolving iron in nitric acid or sulfuric acid. In this process, the concentrations of the acid and iron were prepared so as to form unrelated combinations in the ranges shown in Table 2.

The acid concentration and iron concentration in the sample solutions were obtained by neutralization titration and ICP-AES, respectively. In the following, the neutralization titration method and ICP-AES method are denoted by the term "conventional method."

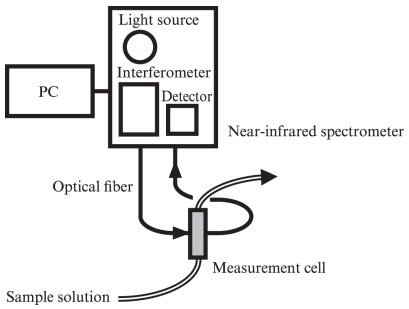

Fig. 1 Schematic diagram of apparatus [7)]

Table 1 Conditions of near-infrared spectrometer measurement [7)]

Measurement probe	Flow through cell
Optical path length	1 mm
Optical path diameter	3 mm φ
Measurement wavenumber	12 500-4 000 cm^{-1}
Resolution	16 cm^{-1}
Cumulative number	256 times
Measurement time	40 seconds
Measurement number	5 times

Table 2 Components and conditions of pickling solutions [7)]

Type of acid	Concentration range (mass%)		Temperatue (°C)
	Acid	Fe	
Sulfuric acid	10〜40	0〜20	60〜80
Nitric acid	5〜20	0〜 8	40〜60

2.2 Comparison of Analytical Values by the NIR and the Conventional Method

The absorption spectrum of the OH bond of first stretching over-tone of water (around 6 800 cm^{-1}) changes accompanying an increase of the ion species in an aqueous solution. Therefore, using this phenomenon, the concentration of an unknown sample was obtained from the relationship between the concentration of a chemical species in an aqueous solution and the absorption spectrum by applying multivariate analysis (PLS: partial least squares regression) based on Eq. (1). The range of the wavenumbers used in the multivariate analysis was optimized so as to obtain the best correlation between the analytical values by the NIR and the analytical values by the conventional method. Because pickling solutions, which are the object of this research, are controlled in a control range of 20°C, there is a possibility that errors may occur in the analytical values by the NIR due to temperature changes. Therefore, the multivariate analysis was performed using all the absorption spectra obtained at the upper and lower limits and intermediate value of the operating temperature so as to avoid the influence of temperature change.

Analytical precision was evaluated by the correlation coefficient and analytical accuracy σd (error of mean square) shown by Eq. (2), comparing the analytical values by the conventional method and the analytical values by the NIR.

$$C=\sum_{i=1}^{n} a_i \cdot x_i \quad \cdots\cdots (1)$$

C: concentration (mass%)
a_i: coefficient
x_i: absorbance (a.u.)

$$\sigma d=\left\{ \sum_{i=1}^{n} (N_i-C_i)^2/n \right\}^{\frac{1}{2}} \quad \cdots\cdots (2)$$

N_i: concentration obtained by the NIR (%)
C_i: concentration obtained by the conventional method (%)

2.3 Actual Pickling Line Tests

An NIR apparatus was installed in an actual pickling line, and tests were carried out under the measurement conditions established in the laboratory. A continuous measurement test for 5 hours with measurements at intervals of approximately 1 minute, and a test in which measurements were performed at intervals of several hours continuously over a 3-day period were performed. In both tests, analysis was performed by the conventional method at appropriate times, and the results were compared with the values by the NIR.

It may be noted that the tests at the actual pickling line were performed with a polypropylene filter having a

hole size of 30 μm installed before the measurement cell because it was not possible to obtain an adequate amount of transmitted light due to the effect of suspended solids such as sludge.

3. Results and Discussion

3.1 Optimization of Analytical Values

Figure 2 shows the near-infrared absorption spectra obtained from simulated solutions with different sulfuric acid concentrations. Although the absorption spectra change corresponding to the sulfuric acid concentration, it is important to select a suitable wavenumber range in order to obtain accurate analytical values by multivariate analysis. Therefore, measurements were performed using various conditions for the wavenumber applied in the multivariate analysis and its range, and the conditions for obtaining accurate analytical values were studied. The wavenumber ranges determined for the respective analytical components were 7 300–6 600 cm^{-1} for sulfuric acid, 10 761–5 361 cm^{-1} for iron in the sulfuric acid, 7 135–5 361 cm^{-1} for nitric acid and 9 450–5 600 cm^{-1} for iron in nitric acid. **Figure 3** shows the correlation between the analytical values by the NIR and the analytical values by the conventional method, obtained under these optimized conditions. Satisfactory results were obtained for all analytical components, as the correlation coefficients were 0.98 or higher.

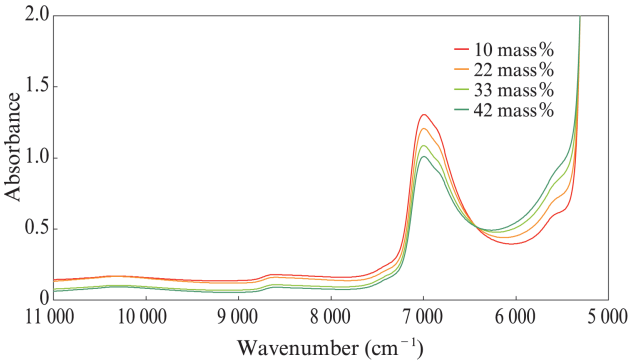

Fig. 2 Near-infrared spectra of aqueous solutions with different sulfuric acid concentration [7)]

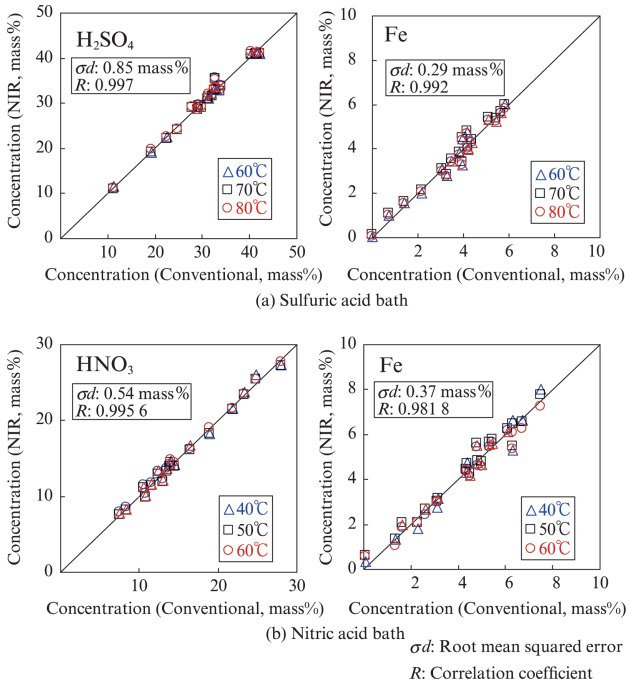

Fig. 3 Comparison of the analytical values of the near-infrared spectrometry and the conventional method [7)]

3.2 Results of Actual Pickling Line Tests

Figure 4 shows the results of continuous measurements of the nitric acid concentration and iron concentration in a nitric acid pickling solution by the NIR apparatus installed in the actual pickling line. The figure also shows the results of analyses of the samples of the pickling solution by the conventional method.

The NIR analytical values were in good agreement with the analytical values by the conventional method. In the continuous measurements at intervals of approximately 1 min, the increase in the acid concentration due to periodic addition of nitric acid was captured precisely, showing that rapid changes in the concentration of the pickling solution can be grasped accurately.

Figure 5 shows the results of an evaluation of long-term stability by measuring the concentrations of sulfuric acid and iron in a sulfuric acid pickling solution by the NIR and the conventional method. The analytical values by the NIR and the conventional method showed extremely good agreement over the 3-day period for both the sulfuric acid concentration and the iron concentration. In all cases, accuracy was 0.5 mass% or less. During the continuous measurement tests at the actual line, the measurement cell and other parts were free of dirt that would affect the analytical values, and stable analytical values could be obtained.

The study described above clarified the fact that it is possible to analyze the concentrations of acid and iron in pickling solutions in steel-making processes rapidly and accurately by near-infrared spectroscopy.

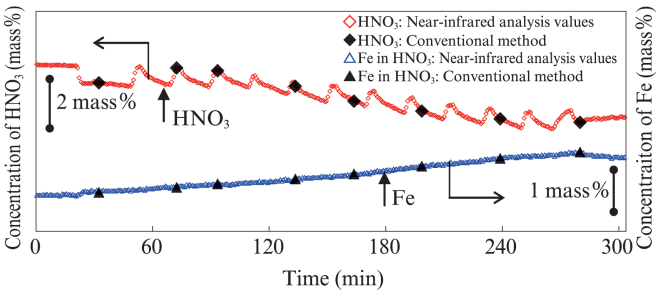

Fig. 4 Results of continuous measurements for actual pickling solution [7)]

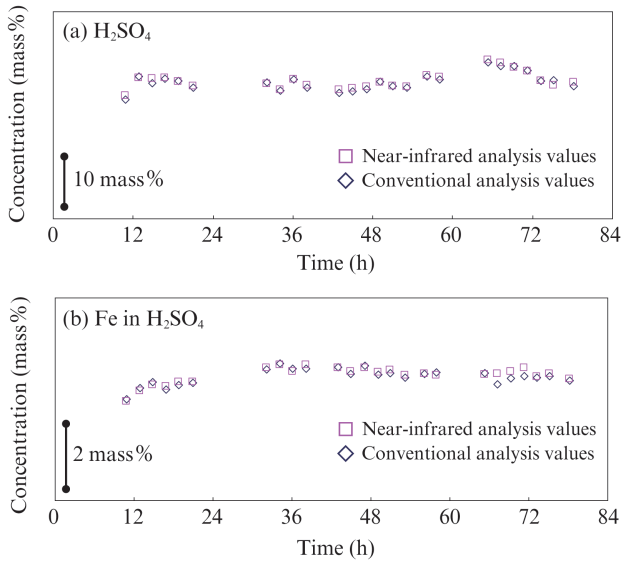

Fig. 5 Long term stability of near-infrared analysis measurement for actual pickling solutions [7)]

4. Conclusion

Near-infrared spectroscopy (NIR) was studied as a control method for the concentration of pickling solutions in steel-making processes. The following knowledge was obtained.

(1) This study clarified the fact that measurement of the acid concentration and iron concentration in pickling solutions is possible by applying multivariate analysis, using the absorption spectra by the NIR under various conditions obtained with simulated pickling solutions and pickling solutions at actual pickling lines.

(2) An on-line measurement test was performed at an actual pickling line. It was found that the analytical values by the NIR and by the conventional method show good agreement, and continuous long-term measurement is possible. The possibility of measurement at intervals of approximately 1 min by this method was also demonstrated.

Based on the results summarized above, rapid and highly accurate measurement of the concentration of the components in pickling solutions in steel-making processes is possible by the NIR.

5. Final Comments

In the future, it is thought that application of near-infrared spectroscopy as an online analysis method for pickling solutions in steel-making processes, and development as a chemical management system which makes it possible to keep the concentration of pickling solutions within the proper range at all times, will make an important contribution to the stable supply of steel products with high surface quality.

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