

R E S E A R C H A N D M A S T E R S P S U N - I S †

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 prod-

acid concentration in the pickling process is extremely important for securing stable product quality. Moreover, because measurement 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 ions³). 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 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 processes⁴⁻⁶). 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.

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.”

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 $6\,800\text{ cm}^{-1}$) 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 (error of mean square) shown by Eq. (2), comparing the analytical values by the conventional method and the analytical values by the NIR.

$$C = a_i \cdot x_i \dots \dots \dots (1)$$

x_i : concentration (mass%)

a_i : coefficient

x_i : absorbance (a.u.)

$$d = \left\{ \frac{(N_i - C_i)^2}{n} \right\}^{\frac{1}{2}} \dots \dots \dots (2)$$

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

