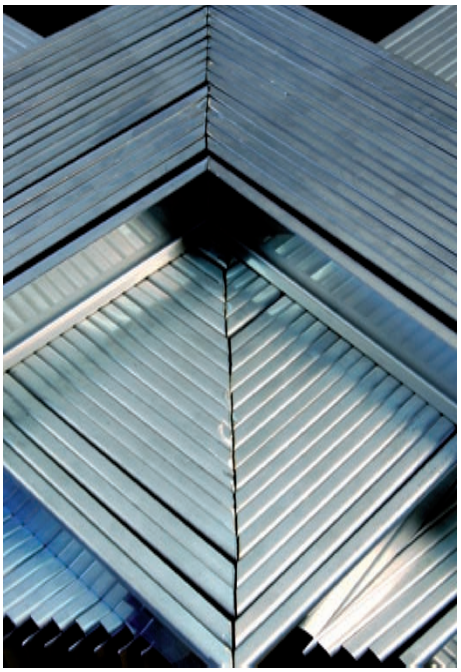
Bath analysis with ProcessLab

Monitoring pickling baths in the steel industry

Scale and rust as steel surface contaminants

Steel is one of the most important starting materials for innumerable products. The world's yearly steel production exceeds 1.3 billion tonnes (1). For some time now, demand has exceeded production, which has led to massive price increases for steel. As a result, new production capacities are being set up and existing plants extended at high investment costs. In order to increase the yield while keeping the quality constant and costs low, each individual step in the production process must be adequately monitored and controlled. An extremely important part of the process is pickling the steel, in which impurities resulting from previous production steps, for example the scale[1] produced during rolling, or any rust already present, are removed and the surface prepared for subsequent process steps. At the same time, interfering annealing colors are removed, the surface being passivated by the formation of a protective layer and in this way protected against further corrosion. Only after the pickling process can steel be formed or its surface treated and, for example, used for the production of automobile or metal construction components.



Surface-treated steel products

Removal of impurities by using pickling baths

The pickling baths used are made up of diluted acids, for example hydrochloric or sulfuric acid, or are mixtures of acids such as HNO_3 / HF or H_2SO_4 / H_3PO_4 / HF. Accelerants and other auxiliary agents are often added to these mixtures to optimize and speed up the process. While pickling removes impurities, the acids used also attack the steel surface and partially dissolve it. This is why it is important that process-relevant parameters such as dwell time, bath temperature and bath composition are controlled and maintained as accurately as possible. This is the only way in which a pickling bath can be operated economically and, above all, in a way that protects both the environment and resources. Physical parameters such as dwell time and bath temperature are easy to monitor, whereas the analysis of bath constituents is usually more complicated and must be carried out in an analytical laboratory.

Analyzing pickling baths with ProcessLab

Steel production is a continuous process that also takes place at night and during weekends. Qualified laboratory personnel are often not available twenty-four hours a day; this can make uninterrupted analytical process control difficult. This is where the Metrohm ProcessLab system for bath analysis opens up completely new possibilities. The easy-to-use ProcessLab analysis system is installed directly in the process area. The only thing that a process worker has to do is bring a bath sample to the ProcessLab and start the system by pressing a single button. ProcessLab analyzes the sample completely automatically. Important process information is available only a few minutes later. This enables on-site process analysis around the clock and results in much more direct and precise process control.

Controlling the important process parameters

Each pickling bath consists of numerous constituents and additives, not all of which are equally relevant to the process. Four of these analytical parameters have a considerable influence on the steel pickling process: the amounts of free and total acid and the iron(II) and iron(III) concentrations. The analyses of these parameters is described in detail below and in Metrohm Application Bulletin 295 (2).

[1] Scale is iron(II, III) oxide that forms on the surface of iron or steel when steel is formed or treated at high temperatures.

The **free acid (FA)** is a measure of the acid still available for pickling. It is determined by potentiometric titration with an NaOH solution to pH 4.2. It is given as the equivalent of an acid present in the bath; in a hydrochloric acid pickling bath, the NaOH consumption corresponds to the free acid in g HCl per liter. During the pickling process in a hydrochloric acid pickling bath, the free acid reacts with the metals to form metal chlorides, which means that the free acid concentration decreases and the bath must be topped up by the addition of concentrated hydrochloric acid.

The **total acid (TA)** corresponds to the total amount of free acid plus the amount of reacted acid. The total acid is determined by titrating with NaOH to pH 8.6. The total consumption of NaOH then corresponds to the total acid equivalent.

The **Fe(II) and Fe(III) contents** in a pickling bath are important process control parameters. They are a measure of the oxidizing power of the pickling bath and therefore have a considerable influence on the pickling time and the quality of the product. Moreover, if the iron contents are too low or too high, pickling becomes ineffective. Fe(II) is frequently determined by titration with potassium permanganate. Unfortunately, $KMnO_4$ has the disadvantage that interfering chlorine and chlorine dioxide are formed in the presence of hydrochloric acid. Another disadvantage is the unstable titer of potassium permanganate solutions. Thus, $KMnO_4$ is not really suitable for routine process analysis. In contrast, cerium(IV) is highly suitable; it is also a strong oxidizing agent and reacts with Fe(II) according to the following equation:

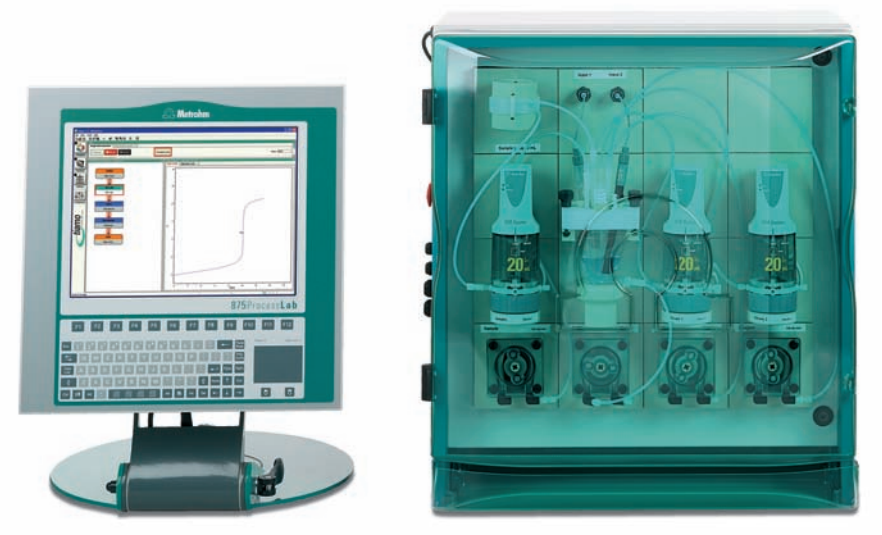
$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

In this reaction, no interfering intermediate products are formed even in the presence of large amounts of chloride and the determination is quantitative. As cerium(IV) solutions have a very stable titer they are ideal for the determination of Fe(II) in pickling baths. The endpoint of the redox titration is detected by means of an ordinary platinum redox electrode.

In addition to the absolute concentrations of Fe(II) and Fe(III), the ratio of the Fe(II) to Fe(III) concentration is also important for an effective pickling process. It should always lie within a certain range. Auxiliary agents such as hydrogen peroxide or nitrites oxidize Fe(II) to Fe(III) and therefore alter the ratio of these two components. Optimal pickling results can only be achieved when the pickling bath has a high oxidizing power with an optimal ratio between Fe(II) and Fe(III).

An overview of the Metrohm analysis system

The ProcessLab system presented here determines fully automatically those parameters that are important for the smooth running of a pickling bath: free acid and total acid as well as the Fe(II) and Fe(III) concentrations. The system is installed



ProcessLab analysis system with analysis module and TFT operating unit with touch-screen.

in the vicinity of the process to be monitored and allows the rapid on-site analysis of various pickling baths. A ProcessLab analysis system always consists of one or several analytical modules adapted to the particular application and a TFT operating unit. With the built-in touch-screen (option) operation becomes even simpler and more comfortable.

Both the operating unit and the analysis module are contained in a robust, splash-water-protected housing and are ideally suitable for use under rough production plant conditions.

The analysis module of the system described here is also of modular construction. A titration vessel with magnetic stirrer, variable and automatic sample metering using a sample loop and an 800 Dosino as well as two 800 Dosinos for the exact addition of the two titrants $Ce(SO_4)_2$ and NaOH are contained in one housing. The peristaltic pumps are used for the automatic addition of reagents and auxiliary agents and for rinsing the titration vessel.

The user only has to take a sample from the bath and bring it to the system. The analysis sequence for the automatic determination of all four parameters is started by pressing a single button. The sample is metered automatically, transferred to the titration vessel and the concentrations of the analytes determined by titration. All the necessary process information is available within only a few minutes, without the bath samples having to be taken to the laboratory for analysis.

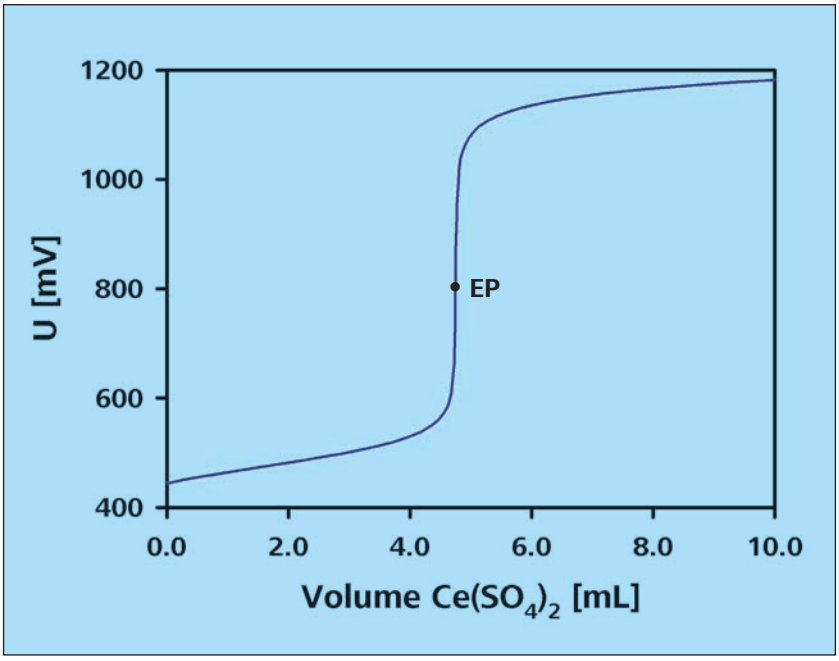
Analysis module equipped with Dosinos, peristaltic pumps and a titration vessel for automatic pickling bath analysis.

Determining the free and total acid

2 mL sample is metered fully automatically, treated with 20 mL potassium fluoride solution (c(KF) = 3 mol/L) to mask the iron, demineralized water is added and the solution then titrated with NaOH solution to pH 4.2. The NaOH consumption corresponds to the amount of free acid in the bath. A further aliquot of the sample is titrated with NaOH solution to pH 8.6; in this case the total amount of NaOH consumed corresponds to the total acid concentration in the bath.

Determining the Fe(II) and Fe(III) concentrations

Demineralized water is placed in the titration vessel and a sample aliquot of 2 mL is added to it automatically. Using a Pt electrode, titration is performed with cerium(IV) sulfate solution (c($Ce(SO_4)_2$) = 0.1 mol/L) to the first endpoint. The Ce(IV) consumption corresponds to the Fe(II) concentration in the pickling bath.



Typical titration curve for the redox-potentiometric Fe(II) determination by titration with cerium(IV) sulfate.

The Fe(III) concentration is then calculated from the free and total acid content taking into account the cerimetrically determined Fe(II) concentration.

The advantages of the ProcessLab system

A single analysis system determines all the relevant bath parameters and collects important process information. The results are available at any time for the subsequent traceability of the process and for making audits easier. The system can also transmit status signals, for example if a predefined limit is infringed or if a fault occurs in the system. Information about the bath content can also be easily transmitted in the form of an analog 4...20 mA signal. The simple process integration is clearly one of the many advantages of the ProcessLab system; information is immediately available to the personnel in the operations center or the process monitoring system. Therefore it is possible to react directly to variations and, if necessary, to take countermeasures. If a variation does occur, the correct amount of fresh acid or auxiliary agent to be added can be calculated with the aid of the included ***«tiamo for ProcessLab»*** software; it is even possible to do the addition fully automatically. Thanks to the rapid availability of the analytical data, the pickling process can be carried out under optimal conditions. On the one hand, this improves the quality of the end product, on the other hand, there results a longer operating period for the pickling bath with simultaneous reduction of its running costs (reduced usage of chemicals). As a result of the cost savings due to more efficient bath control and higher-quality end products, a ProcessLab system normally has a pay-back time of less than three years.

Summary

The quality of the end product is considerably influenced by how well and reproducibly the individual process steps are carried out. The Metrohm ProcessLab system described here is used for fully automatic on-site analysis of all the relevant process parameters of a steel pickling bath. This means that all the analytical data is available directly after sampling. The amount of bath additives to be added can be calculated automatically and, if required, also added automatically. The system offers numerous possibilities for process integration, guaranteeing the relevant information is quickly available wherever it is required.

Thanks to ProcessLab, pickling baths can be used more economically and ecologically and operating and disposal costs are considerably reduced. This also makes a particular contribution to protecting both resources and the environment.

References

(1) International Iron and Steel Institute (IISI), data for 2007, www.worldsteel.org

(2) Metrohm Application Bulletin AB 295: Determination of Fe^{2+}, Fe^{3+}, total and free acid in an etching bath (steel industry), Metrohm AG, Switzerland

Further reading

Monograph: Practical titration – training manual for titrimetric volumetric analysis, 2005, 164 pages, Metrohm AG, Switzerland

Prozessbegleitende Analytik in der Galvanotechnik, T. W. Jelinek, 1999, 440 pages, Eugen G. Leuze Verlag, Saulgau