Application Note AN-PAN-1019

Online analysis of acids and iron in pickling baths

In the galvanic industry, pickling baths are utilized to clean and remove most oxides from various steel surfaces, as well as to passivate the surface to prevent corrosion.

It is crucial to maintain specific limits for the Fe^{2+}/Fe^{3+} and free acid/total acid ratios to ensure the chemical bath remains in optimal working condition. The proper composition of the baths directly affects the quality of the final products. By maintaining these parameters within optimal ranges, the quality of the resulting products is improved, and production costs are lowered due to decreased reagent consumption.

This Process Application Note presents a method to regularly monitor the acid and iron composition in pickling baths online to ensure an even cleaning process by using a process analyzer from Metrohm Process Analytics.

INTRODUCTION

Countless products begin with steel, which is one of the most essential raw materials.

Hot-dip galvanizing (Figure 1) is a process that involves coating steel (or iron) with a layer of zinc to protect it from corrosion [1]. An extremely important part of steel production is the **pickling process**, in which impurities such as mill scale produced during high-temperature rolling are removed and the surface prepared for subsequent process steps. At the same time, interfering annealing colors are removed while the surface is passivated by the formation of a protective layer to protect against further corrosion.

The pickling baths used are made up of diluted acids and can vary in composition depending on the grade of steel being treated. In most cases, hydrochloric or sulfuric acid (HCl, H_2SO_4) are used, or mixtures of acids such as HNO_3/HF or H_2SO_4/H_3PO_4/HF. While pickling removes impurities, the acids used also attack the steel surface and partially dissolve it. This over-pickling of the base steel can result in the **metal pitting** which leads to an undesirable rough, blistered coating in the following galvanizing steps, and also causes *excessive consumption* of the pickling acid. Dissolved iron in the form of iron oxides present in the metal oxide scale affects the pickling rate of steel as iron concentrations increase. Therefore, it is important that process-relevant parameters such as **bath composition** are controlled and maintained as accurately as possible to reduce the overconsumption of pickling chemicals while keeping the quality of the product constant.

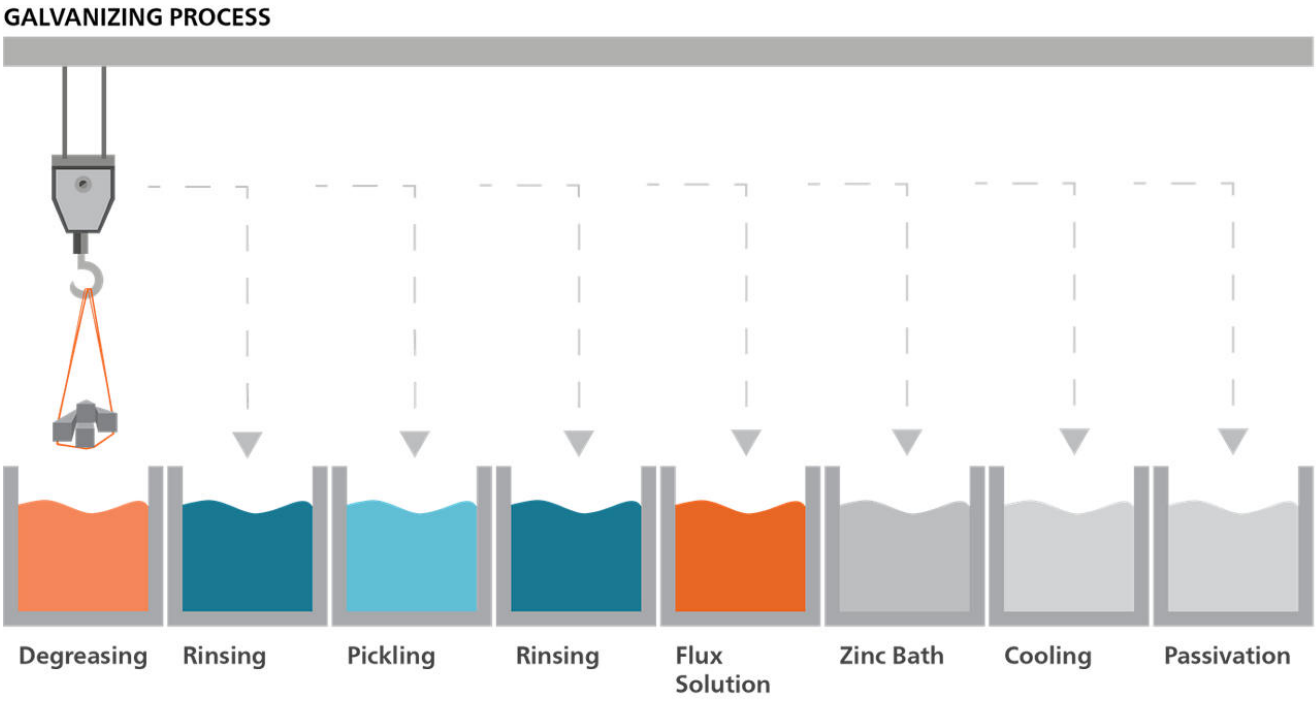

Figure 1. Illustration of the multi-step hot-dip galvanizing process. The pickling bath is shown in light blue.

Pickling is a highly corrosive process, and if the bath is not monitored carefully, it can lead to issues in the resulting product. Continuous online monitoring of **free and total acids** and **iron content** satisfies this requirement and as a result, pickling baths can be used more economically and ecologically. Thus, operating and chemical disposal costs are considerably reduced.

Metrohm Process Analytics offers a multi-parameter process analyzer that is suitable for the simultaneous analysis of Fe^{2+}/Fe^{3+} and free acid/total acid ratio over a wide concentration range—the **2060 TI Process Analyzer** (**Figure 2**).

Figure 2. 2060 TI Process Analyzer for the online analysis of critical quality parameters in pickling baths using the method of titration.

APPLICATION

Total acids, individual acids, and iron (i.e., HCl, H_2SO_4, HNO_3, HF, Fe_2^+, and Fe^{3+}) were analyzed using accurate titration methods. Performance monitoring of pickling baths is possible with the use of Metrohm process analyzers, either the 2026 HD Titrolyzer or the 2060 TI Process Analyzer, depending on whether single- or multi-parameter measurements are required.

Table 1. Parameters and their concentration ranges in pickling baths.

Parameters	Concentration [g/L]
HCl	15–250
Fe^{2+}	10–200
Fe^{3+}	1–20
HNO_3	10–250
HF	0–100
H_2SO_4	0–300

REMARKS

A settler (Figure 3) can be used as a robust preconditioning system to remove solids and particles from the liquid sample prior to the analysis.

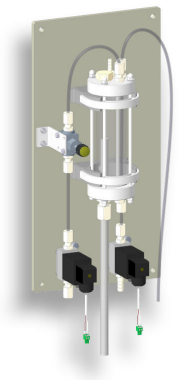

Figure 3. Settler unit for removal of particles.

CONCLUSION

During steel production, the pickling process prepares the steel surface for subsequent finishing steps. These pickling baths contain combinations of HCl, H_2SO_4, HNO_3, HF, H_3PO_4, Fe^{2+}, and Fe^{3+}. For reproducible surface treatment, the bath composition must be continuously monitored. This is best done online with titration by using a rugged Metrohm process analyzer such as the 2060 TI Process Analyzer. By supplying real-time information to the industrial control system (such as DCS or PLC) with an online process analyzer, downtimes are reduced, bath composition is optimized, and costly company assets are safeguarded.

REFERENCES

1. What is the HDG Process?. American Galvanizers Association. https://galvanizeit.org/hot-dip-galvanizing/hdg-process (accessed 2023-05-08).

RELATED APPLICATION NOTES

AN-PAN-1006 Determination of zinc, sulfuric acid and iron

AN-PAN-1012 Online analysis of nickel ion & hypophosphite content

AN-PAN-1018 Determination of acids, bases and aluminum: galvanic industry – metal surface treatment

OTHER RELATED DOCUMENTS

WP-076 Process analyzers as proactive solutions for online corrosion monitoring

BENEFITS FOR ONLINE PROCESS ANALYSIS

- Enhanced reproducibility, production rates, and profitability (less waste).
- Fully automated diagnostics – automatic alarms for when samples are out of specified concentration parameters.
- Efficient steel pickling at a high level of quality by constantly monitoring the processing baths.
- Avoid unnecessary costs by reducing the amount of time required to achieve the desired pickling results.

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CONFIGURATION

2060 Process Analyzer

The 2060 Process Analyzer is an online wet chemistry analyzer that is suitable for countless applications. This process analyzer offers a new modularity concept consisting of a central platform, which is called a «basic cabinet».

The basic cabinet consists of two parts. The upper part contains a touch screen and an industrial PC. The lower part contains the flexible wet part where the hardware for the actual analysis is housed. If the basic wet part capacity is not sufficient enough to solve an analytical challenge, then the basic cabinet can be expanded to up to four additional wet part cabinets to ensure enough space to solve even the most challenging applications. The additional cabinets can be configured in such a way that each wet part cabinet can be combined with a reagent cabinet with integrated (non-contact) level detection to increase analyzer uptime.

The 2060 process analyzer offers different wet chem techniques: titration, Karl Fischer titration, photometry, direct measurement and standard additions methods.

To meet all project requirements (or to meet all your needs) sample preconditioning systems can be provided to guarantee a robust analytical solution. We can provide any sample preconditioning system, such as cooling or heating, pressure reduction and degassing, filtration, and many more.