

# Influence of Iron in Pickling Solution of Sulfuric Acid on its Activity

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Parameters of deactivation of  $H_2SO_4$  pickling bath, resulting from the presence of iron ions, were determined on the basis of laboratory pickling tests of steel sheets prior to enamelling. The critical value of mass loss of sheet at pickling was determined by means of artificially inoculated pickling solutions increasingly saturated by carbonyl iron and in gradually saturated solution by means of iron from steel sheets. Relationship between the increase of iron amount in pickling solution and the amount of carbonyl iron was determined by mathematical regression analysis.

Pretreatment of steel sheets prior to enamelling is carried out by the classical chemical procedure which includes an alkaline degreasing, pickling in inorganic acids, neutralization, rinsing and Ni-flashing [1, 2]. Pickling prior to enamelling follows the purpose to prepare the surface of sheets for "anchorage" of porcelain enamels in contrast to the classical pickling aimed at the removal of  $Fe_xO_y$  oxides. For example, at the direct-on white enamelling process a mass loss from the sheet surface, amounting to 20–50 g  $m^{-2}$ , is required. This process removes a layer 5–10  $\mu m$  thick [3].

Minimally 90 % of pickled products are treated in inorganic acids, particularly in  $H_2SO_4$ , HCl, and  $HNO_3$  or in the mixture of acids. It is obvious that the selection of the pickling bath has a substantial influence. Increase of pickling intensity in  $H_2SO_4$  can be controlled by suitable setting of bath temperature, since the volatility of the acid slightly increases with rising temperature [4]. On the other hand, it appears more reasonable to control the pickling process in HCl by the change of its concentration on the grounds of sufficient mass losses and the high volatility of this acid [4]. Electron-microscopic examination indicates [5] that the sheets pickled in  $H_2SO_4$  have uniformly wrinkled surface with fine morphology. Pickling with  $H_2SO_4$  produces various crystallohydrates of  $FeSO_4$  ( $FeSO_4 \cdot H_2O$ ,  $FeSO_4 \cdot 4H_2O$ ,  $FeSO_4 \cdot 7H_2O$ ) according to the degree of saturation of solution with iron ions [6].

The presented paper concentrates on the analysis of pickling activity and gradual wasting of  $H_2SO_4$  pickling bath in dependence on its saturation

with iron ions. Analysis is based on experimental results obtained at pickling of deep-drawing cold rolled steel sheets intended for enamelling.

## EXPERIMENTAL

Cold rolled steel sheets produced by East Slovakian Ironworks (Košice) according to CSN 411 310 with chemical components given in Table 1 were used. Pickling efficiency tests were performed on specimens of dimensions 50 mm x 100 mm and thickness 1 mm, intended for enamelling.

Microstructure of material is ferritic, homogeneous, composed of polyhedral, very slightly elongated grains of medium size 20  $\mu m$ . Cementite phase creates chains in the form of polyhedral configurations in the direction of rolling. There are cavities among the cementite particles, created during the process of cold forming, as a result of crushing of these hard phases.

The constant starting state of sheet specimen surfaces was achieved by two-stage degreasing procedure. The first stage consisted in preliminary degreasing of specimens in organic solvents after which followed the galvanic degreasing in electrolyte, containing 10 g of SYNALOD 3024 in 1  $dm^3$  of  $H_2O$ , lasting for 2 min at 6 V and 50 A  $m^{-2}$ . SYNALOD is a white, crystalline, water-soluble substance containing metasilicates, carbonates, pyrophosphates, and detergents.

Pickling efficiency tests were carried out using 1  $dm^3$  of 1.13 M- $H_2SO_4$  considered as stock solution in an apparatus with secured reproducible oxygen content in solution. Pickling time amounted to 6 min at the temperature 60 °C. Mean mass losses per 1  $m^2$  area of sheet surface at pickling were calculated from three specimens.

**Table 1.** Content of Elements in Steel Sheets

Element	C	Mn	Si	Cu	S	P	Al
w/%	0.04	0.25	0.04	0.016	0.010	0.011	0.035

## RESULTS AND DISCUSSION

## Influence of the Amount of Carbonyl Iron in Acidic Solution on its Activity

Pickling activity of acid was determined by measurement of mass loss of sheet specimens and analytical determination of the increase of iron amount in the set of artificially inoculated  $\text{H}_2\text{SO}_4$  solutions after pickling. The pickling solutions were prepared by addition of carbonyl iron in amounts 1, 5, 10, 20, 22, 25, and 30 g into  $1 \text{ dm}^3$  of  $1.13 \text{ M-H}_2\text{SO}_4$ .

of incipient oversaturation of solution with regard to  $\text{Fe}^{2+}$  concentration. Table 2, however, shows that with regard to appreciably very continuous character of the change of mass loss values this method cannot be used for unambiguous determination of the limit, beyond which the acid loses its activity.

Pickling activity of acid was confirmed by qualitative and quantitative determination of Fe concentration in solutions after pickling. Determination of the total Fe content in the solutions 1 up to 9 (Table 2) was carried out photometrically with KSCN, by oxidation of  $\text{Fe}^{2+}$  ions by means of

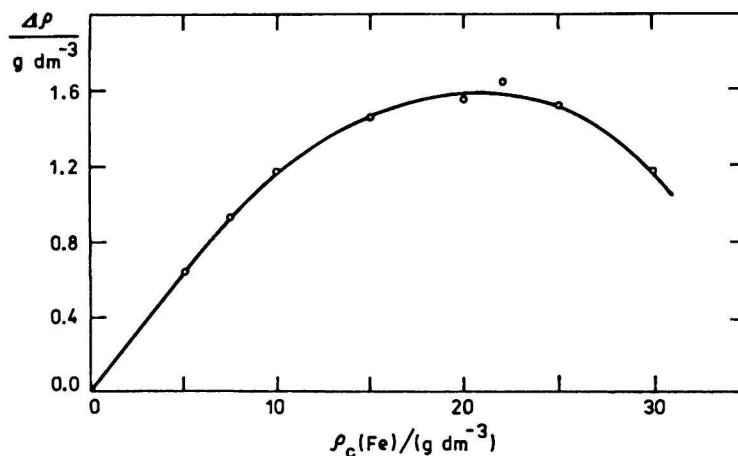


Fig. 1. Dependence of the difference of the increase of Fe concentration in the stock solution ( $1.13 \text{ M-H}_2\text{SO}_4$ ) on the concentration of carbonyl Fe in the pickling bath.

Mass loss measurements indicated that some decrease of values was recorded starting from the pickling solution containing carbonyl iron in amount exceeding  $20 \text{ g dm}^{-3}$ , suggesting the state

$(\text{NH}_4)_2\text{S}_2\text{O}_8$  to  $\text{Fe}^{3+}$  ions. With regard to the short pickling time (6 min) and secured reproducible oxygen content the presence of ferric ions is negligible.

Table 2. Results of Measurements of Fe Concentration after Pickling

n	Pickling solution		Solution after pickling			$\frac{\rho_p^n(\text{Fe}) - \rho_c(\text{Fe})}{\text{g dm}^{-3}}$	$\frac{\Delta\rho = \rho_p^n(\text{Fe}) - \rho_p^1(\text{Fe})}{\text{g dm}^{-3}}$
	$\frac{\rho_c(\text{Fe})}{\text{g dm}^{-3}}$	$\frac{\omega}{\text{g m}^{-2}}$	$\frac{\rho(\text{H}_2\text{SO}_4)}{\text{g dm}^{-3}}$	$\frac{\rho_a(\text{Fe})}{\text{g dm}^{-3}}$	Absorbance $A_{500}$		
Standard	1	—	—	—	0.011	—	—
1	0	8.4	107.5	2.0	0.022	2.0	0
2	5	8.3	97.62	7.64	0.084	2.64	0.64
3	7.5	8.2	92.93	10.32	0.112	2.92	0.92
4	10	8.5	87.93	13.18	0.145	3.18	1.18
5	15	8.2	78.94	14.44	0.201	3.44	1.44
6	20	8.1	69.77	23.55	0.259	3.55	1.55
7	22	7.6	66.13	25.63	0.282	3.63	1.63
8	25	7.4	61.12	28.49	0.313	3.49	1.49
9	30	6.8	52.91	33.18	0.365	3.18	1.18

$\rho(\text{pickling } 1.13 \text{ M-H}_2\text{SO}_4) = 111 \text{ g dm}^{-3}$ ,  $\rho_c(\text{Fe})$  - concentration of carbonyl Fe in solution,  $\rho_a(\text{Fe})$  - total concentration of Fe after pickling,  $\rho_p^n(\text{Fe})$  - values of the increase of Fe concentration in the  $n$ th solution,  $\Delta\rho$  - difference of the increase of Fe concentration compared to the first solution ( $\rho_p^1 = 2.0$ ),  $\omega$  - area density of mass loss of sheets.

Fig. 1 shows the typical curve of saturation of solution with  $\text{Fe}^{2+}$  ions described by the following parabolic equation of the nonsymmetrical type

$$\Delta\rho = 15.3 \times 10^{-2} \rho_c(\text{Fe}) - 0.37 \times 10^{-2} [\rho_c(\text{Fe})]^2$$

where  $\Delta\rho/(\text{g dm}^{-3})$  is the difference of increments of Fe concentration compared with the stock solution (1.13 M- $\text{H}_2\text{SO}_4$ ) without Fe,  $\rho_c(\text{Fe})$  concentration of carbonyl Fe in the pickling solution.

The behaviour of the curve very distinctly points to the change of activity of sulfuric acid induced by the presence of artificially introduced carbonyl Fe. Linear dependence suggesting the stability of the pickling process extends up to the concentration approx. 6.5 g of carbonyl Fe in 1  $\text{dm}^3$  of solution. Afterwards the pickling activity of acid gradually diminishes up to the value approximately  $\rho_c(\text{Fe}) = 20 \text{ g dm}^{-3}$ . Inflexion point observed at this value represents the loss of active pickling capabilities. This is demonstrated by the decrease of mass loss of specimen.

were subjected to successive pickling in 1  $\text{dm}^3$  of 1.13 M- $\text{H}_2\text{SO}_4$  (the stock solution), for 6 min each, at the temperature 70 °C. Constant conditions were ensured by keeping the pickling bath in a calorimeter while appropriate instrumental arrangement prevented the evaporation of acid. 1  $\text{dm}^3$  of solution was used for pickling of approximately 500 specimens. This experiment represents a model of the pickling process under practical conditions.

The relationship in Fig. 2 shows that the area density of mass loss ( $\omega$ ) of specimen up to the concentration value of 1 g Fe in 1  $\text{dm}^3$  of solution is somewhat higher than the subsequent first plateau around the medium value of  $\omega = 10.4 \text{ g m}^{-2}$  with the dispersion variance  $\pm 9.6 \%$ , which extends up to the value of 7 g Fe in 1  $\text{dm}^3$  of solution. Next plateau with slightly declining tendency terminates at  $\rho(\text{Fe}) = 18 \text{ g dm}^{-3}$  and its average value of the area density of mass loss equal to  $6.8 \text{ g m}^{-2}$  represents about 35 % decrease.

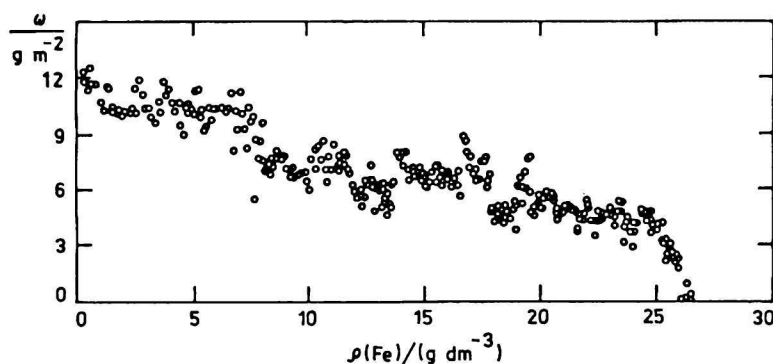


Fig. 2. Dependence of the area density of mass loss of sheets on the amount of Fe dissolved in the stock solution.

Results of measurements indicate that from the viewpoint of evaluation of the influence of dissolved Fe on the capabilities of pickling solutions more accurate picture is obtained on the basis of dependence of difference of increments of Fe concentration compared with the mass losses of specimens, since this relationship reacts more sensitively mainly in the sphere of saturation of acid. Dependence of the mass loss records, however, only the final state – the oversaturation effect.

### Influence of Fe Dissolved by Pickling on the Activity of Acid

An extensive experiment was carried out to determine the dependence of mass loss of specimen on the amount of dissolved Fe, present in solution as a product of pickling. Sheet specimens with dimensions 50 mm x 100 mm x 1 mm

Accuracy of experimental results was verified by analysis of the amount of dissolved Fe in used stock solution by means of photometric and AAS methods. The colloidal turbidity of  $\text{Fe}(\text{OH})_3$  was observed in the solution. The obtained solution was filtered and the total concentration of iron was determined in the filtrate  $\rho(\text{Fe}) = 26.08 \text{ g dm}^{-3}$  and in the insoluble portion  $\rho(\text{Fe}^{3+}) = 0.42 \text{ g dm}^{-3}$ . The total area density of mass loss of all 500 specimens was  $26.65 \text{ g m}^{-2}$ . These results indicate a hundred per cent concordance between the mass loss of samples and total concentration of Fe in the solution.

### CONCLUSION

The conditions for formation of  $\text{FeSO}_4$  hydrates are produced in three-phase system  $\text{H}_2\text{SO}_4\text{—H}_2\text{O—FeSO}_4$  according to the saturation degree

and the solution temperature. Undesirable crystallization of  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  results in the loss of acid activity. Process of pickling stops already before the complete exploitation of  $\text{H}_2\text{SO}_4$ , since the dissolution rate of iron is small at low  $\text{H}_2\text{SO}_4$  concentrations. In our experiment after approx. 55 % utilization of original 1.13 M- $\text{H}_2\text{SO}_4$  the mass loss of sheets decreased below the acceptable value.

Successive pickling of steel sheet specimens in 1 dm<sup>3</sup> of 1.13 M- $\text{H}_2\text{SO}_4$  showed that up to the value equal to 7 g of Fe in solution the mass loss of specimens remains unchanged. Gradual saturation of acid by  $\text{Fe}^{2+}$  ions from sheet specimens up to 18 g of Fe per 1 dm<sup>3</sup> results in the decrease of the mass loss by as much as 35 %. Additional

pickling causes further intensive saturation and wasting of acid.

## REFERENCES

1. Thielmann, C. C. R., *Emailtechnik* No. 11–12, 6 (1988).
2. Hoffmann, H., *Email—Metal* No. 6, 36 (1970).
3. Hoens, M. F. A. and van der Vliet, W. E., *Mitt. des Vereins Deutscher Emailfach Leute E. V.* 34 (10), 125 (1986).
4. Šturc, I. et al., *Moření oceli*. (Pickling of Steel.) P. 124. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1985.
5. Nižník, Š., *Hutn. Listy* 45, 345 (1990).
6. Moore, W. I., *Fyzikální chemie*. (Physical Chemistry.) P. 276. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1979.

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