



Laboratory-scale simulation of industrial neutral electrolytic pickling as a bipolar system—Parameters affecting indirect polarization pickling of annealed stainless steel

Teemu Tuovinen¹ | Tuomas Vielma | Ulla Lassi¹

University of Oulu, Oulu, Finland

Correspondence

Teemu Tuovinen, University of Oulu, PO Box 8000, FI-90014 Oulu, Finland.
Email: teemu.tuovinen@oulu.fi

Funding information

Symbiosis of Metals Production and Nature (SYMMET)

Abstract

As the production of stainless steel increases, environmental concerns due to an increasing demand of production capacity, require an efficient use of energy and materials. Efficient removal of otherwise slow-to-dissolve chromium oxide layer can be achieved with electrochemical pre-pickling before final mixed acid pickling. Neutral electrolytic pickling can be used to rapidly dissolve chromium oxides but suffers from low current efficiency of both the reaction and the system. In order to study the effect of critical parameters for the current efficiency of the system, a pickling device was assembled. A system current efficiency factorial analysis of bipolar neutral electrolytic pickling was conducted for temperature, electrolyte concentration, cell potential, and electrode-to-sample distance. Lowering the concentration of electrolytes shows potential to increase current efficiency significantly as conductivity can be used to reduce electrode-to-electrode short-circuiting, which is the biggest cause of decreased efficiency in neutral electrolytic pickling. Increasing the temperature has a positive effect on efficiency, despite increased conductivity, possibly from increasing reaction kinetics.

KEYWORDS

bipolar electrode, current efficiency, factorial analysis, neutral electrochemical pickling, stainless steel

1 | INTRODUCTION

Stainless steel is the most important synthetic metal alloy used in the world, and global demand has been forecasted to keep increasing.¹ During production, stainless steel is heated, and a scale consisting of several elements including chromium, iron, manganese, nickel, silica, and others, is formed, depending on the alloying of stainless steel.²⁻⁵ At first, the oxide phase mainly consists of chromium oxide, with lesser amounts of other oxides as pointed out by an anonymous peer reviewer. As the scale thickens, phase of mixed oxides is formed. Finally, the exponential growth of iron oxide

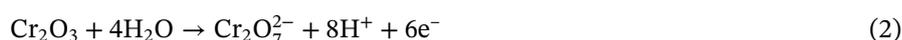
This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

© 2020 The Authors. *Engineering Reports* published by John Wiley & Sons, Ltd.

shifts chromium oxide to the inner layer.⁶ During annealing, chromium oxide remains in the main phase as heating time remains relatively short.^{4,7-9}

Neutral electrolytic pickling, developed in Austria by the Ruthner company in the 1960s, utilizes electrochemistry for the rapid dissolution of scale as a pre-pickling step for final mixed acid pickling.^{3,6,10,11} The process is also known as the Ruthner Neolyte Process or neutral electrochemical pickling.^{3,12} A solution of sodium sulfate, from 15 to 20 wt%, is used as a self-regenerating electrolyte, but unlike the name suggests, the pH of the electrolyte is often adjusted to slightly acidic.^{3,12,13}

The mechanism of neutral electrolytic pickling remained under debate for over 30 years after the first patent was registered, but several researchers^{3,9,11,13-15} have reached a consensus that it is anodic dissolution. Hildén et al⁹ described a detailed mechanism consisting of the dissolution of chromium and manganese oxides at the transpassive stage, followed by the dissolution of iron oxides at prolonged polarization as the most likely mechanism. Main reactions^{9,10,14} for neutral electrolyte pickling can be seen in Equations (1)-(3). The gas-forming side reactions can be seen in Equations (4) and (5). They consume up to 90% of the current during pickling.¹¹



Published research concerning neutral electrolytic pickling remains sparse. Li et al¹⁴ studied the reaction mechanism for hot-rolled samples and reported an additional current peak at the active stage, as well as a peak at the transpassive stage observed for annealed samples. They concluded that pickling in the active stage would be more efficient for hot-rolled samples.

Shapovalov et al¹³ studied the process at the industrial scale pickling line, and Ipek et al reported current efficiency studies for the geometry of the system^{16,17} and the effect of gas formation.¹⁸ The results of Ipek et al^{11,16-18} as well as Shapovalov et al^{13,19} have been used to verify the modeling approach to neutral electrolytic pickling by Ipek et al^{16-18,20,21} and Vynnycky and Ipek.²²⁻²⁴

Ipek et al¹¹ analyzed the effects of temperature, pH, and current density on reactions' current efficiency and concluded that low pH, high temperature, and high current densities are preferable. Ipek et al¹¹ speculated that temperature and current density increased efficiency by increasing reaction kinetics. However, the results of Matsubashi et al^{3,15} contradict the effect of pH as they observed only a slight increase in reaction efficiency. A low pH might change the electrochemical dissolution mechanism of pickling with acidic dissolution of oxides,²⁵ indicated by a loss of efficiency as current density is raised.

Hildén et al⁹ observed that the current density limit is 10 mA cm⁻² for gas evolution and 0.1 mA cm⁻² for oxide layer dissolution. Industrial pickling line current densities, 50-300 mA cm⁻², far exceed the limit of gas evolution to increase the otherwise impractically slow rate of dissolution.^{11,13}

The bipolar system differs from the directly polarized, or classical system.²⁶ The basic bipolar system can be seen in Figure 1A. The electric current passing from cathode to anode through the metallic conductor between them causes a polarization of the metal. The metal acts as a cathode and anode at the same time, leading to bipolarity. For clarity, this electrode is referred to as a bipolar electrode, a sample or steel line, even as it is, by definition, an electrode as noted by an anonymous peer reviewer. Unlike the classical electrolytic system, where a sample acts as a working electrode, there is no contact between the bipolarized electrode and the power source. In Figure 1B, a variation of the classical electrochemical system is presented for comparison.

In industrial pickling, the stainless steel strip travels at high speed. This causes up-and-down movement at the pickling line that can cause dangerous spikes in the electric current if it is applied by direct contact.¹³ To counteract this, the steel strip runs between sets of electrodes that indirectly bipolarize the stainless steel strip as shown in Figure 2.

In a bipolar neutral electrochemical pickling system, the current efficiency is decreased because of electrode-to-electrode short-circuiting. From the total current only about 20%-30%⁶⁻⁸ goes through the steel strip leaving total current efficiency as low as 2%-6% when combined with the effect of the current lost to side reactions.¹¹

FIGURE 1 (A) Basic bipolar system. The passing electric current bipolarizes the sample. (B) A variation of the classical electrochemical system. The sample acts as working electrode

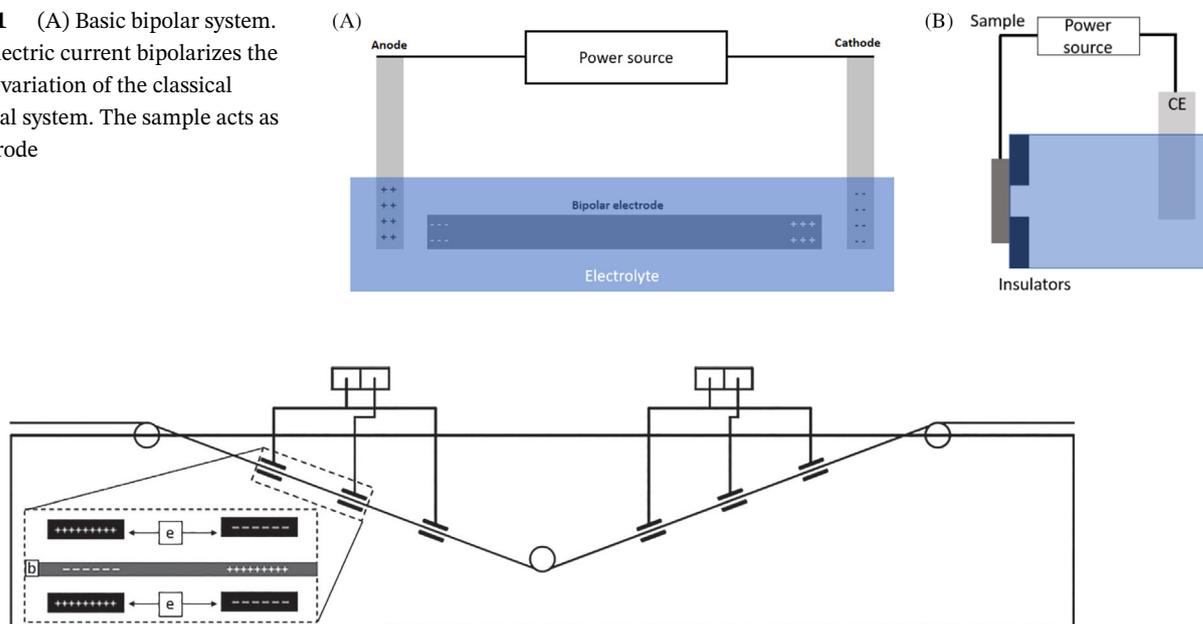


FIGURE 2 Industrial Neolyte Process pickling line, where the steel strip (b) has several polarizations (+/−) that are opposite to the electrode (e) polarities

For these reasons, there is a need for deeper understanding of the industrial electrochemical pickling system as a bipolar phenomenon. To research the Ruthner Neolyte Process in the context of a bipolar system, a laboratory scale pickling device was constructed. Temperature and current density have a critical role in the current efficiency of the dissolution reactions, but the effect for the current efficiency of system remains unquantified. At phase boundaries, lower conductivity of electrolytes causes a drop of 96% of cells' potential,¹³ but increasing the conductivity should increase electrode-to-electrode short-circuiting.²⁶ The effects of temperature and potential have remained unquantified. The effect of electrolyte concentration was modeled by Ipek et al¹⁶ but was not part of the experimental research, having both asymptotic limitations and an apparent typing error at the results.

Therefore, a factorial study was conducted to quantify the effects these factors have on a bipolar system. The results help to evaluate crucial factors for industrial scale pickling plants and optimize pickling conditions to maximize the end results of pickling. As neutral electrochemical pickling effectiveness correlates to decreases in mixed acid pickling time,¹¹ the final mixed acid pickling is omitted from scope of this research in order to focus on the electrochemical pickling system, despite suggestions from a peer reviewer. This research is part of a wider study of neutral electrochemical pickling as the majority of published research is almost two decades old or concerning other parts of the pickling process, such as the utilization of pickling sludge,^{27,28} final (mixed) acid pickling and possible replacement methods,^{29–35} or the effect of pickling on the corrosion of stainless steel.^{7,36,37} As the Ruthner Neolyte Process is widely used,^{3,6,28,38} even a small increase in efficiency leads to both a local and global reduction of steel industries' energy requirements.

2 | EXPERIMENTAL SECTION

Cold-rolled and annealed stainless steel process samples of ASTM304 were received from the steel mill at Outokumpu Stainless Oy Tornio, Finland. The nominal composition of the sample, as reported by the producer, is presented in Table 1. Samples of 1.5 mm thickness were cut with a Struers Secotom-10 precision saw (Struers, Denmark) into 1.5 cm × 5 cm pieces using a 50A20 aluminum oxide cut-off wheel. The maximum active area was 7.5 cm² per side of the sample, and

TABLE 1 Weight percent elemental composition the of ASTM304 stainless steel as declared by the producer

Cr	Ni	Mn _{max}	C	Si _{max}
18.1	8.1	2	0.04	1

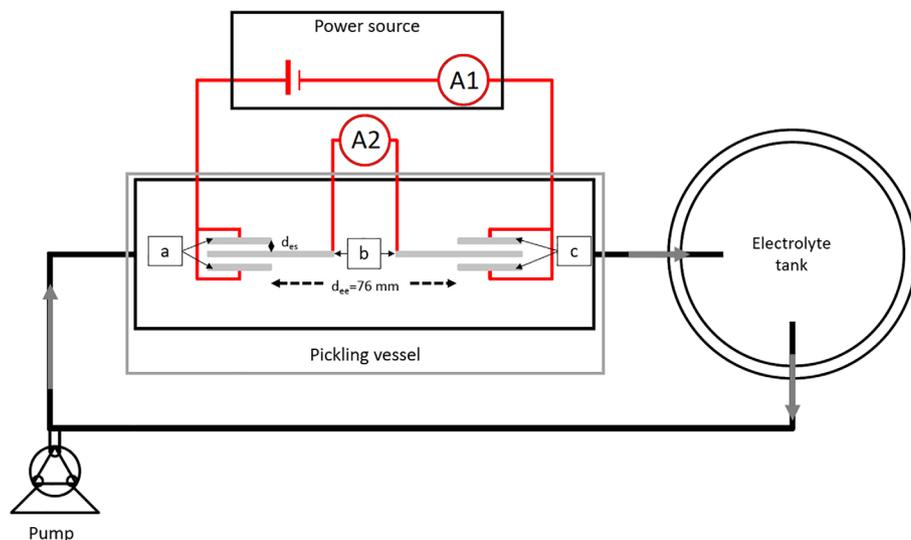


FIGURE 3 Measurement system for bipolar pickling. Electrolyte is pumped from the tank to the pickling vessel, and the flow is marked with gray arrows. The vessel is marked with a gray rectangle. From the pickling vessel, the electrolyte flows back to the tank. The power source, marked with a black rectangle, is coupled to the pickling vessel. Amperometers A1 and A2 measure the current inserted into the system and passing sample. Anodes (A) and cathodes (C) surround samples (B) in distance d_{es} , polarizing samples indirectly. Electrode-to-electrode distance (d_{ee}) is 76 mm

the total area was used in current density calculations, despite the uneven distribution of the current in the samples. Electrodes were cut from grade-1 titanium with dimensions of 30 mm × 25 mm × 1.5 mm.

The samples were electrochemically pickled with device consisting of three parts, a pump, the pickling vessel and, a power source as the schematic illustrates in Figure 3. This bipolar neutral electrochemical pickling system will be referred as the system and systems current efficiency refers to the efficiency of the device.

Sodium sulfate (Na_2SO_4 , Honeywell, purity ≥ 99.1) solution was used as the electrolyte and pumped with a Watson Marlow 520DU (Watson-Marlow, United Kingdom) peristaltic pump from the electrolyte tank to the pickling vessel milled from polytetrafluoroethylene (PTFE). The flow rate was kept at 800 mL min^{-1} , decreasing the number of gas bubbles at the sample and electrodes. The electrolyte tank was kept at a constant temperature and stirred with a magnetic stirrer-heating unit.

Samples and electrodes were fastened to the pickling vessel cover made from polyvinyl chloride (PVC). Both sets of electrodes were fastened with steel plates and threaded rods that doubled as parallel circuiting and allowed adjustment of the electrodes-to-sample distance (d_{es}). The distance between electrodes (d_{ee}) was fixed. Electrodes were positioned around the sample, as show in Figure 3, with an area of 25 mm × 25 mm submerged in the electrolyte solution. Samples were dispensed with plastic holders from one side and galvanized steel holders from the other. The iron holders were connected to each other via a recording amperometer (BAHCO Multimeter BMMTRS1, France), labeled A2 in Figure 3. This allowed both the measurement of the current passing through the samples and formation of a single bipolar electrode from the samples. One sample acted as anodic end of and the other as cathodic end of the bipolar electrode. The sample that was first polarized as a cathode will be referred as the sample in the future.

Keysight E36312A (Keysight, Malaysia) was used as the power source, and the amperometer, labeled A1 in Figure 3, for recording of total current of the system as the device can record both output voltage and current. Used pulse settings can be seen in Table 2, with total cell voltage being variable in factorial analysis. The average current of each pulse was calculated

Electrode polarization	Sample polarization	Time (s)
Anodic	Cathodic	5
Cathodic	Anodic	5
Anodic	Cathodic	10
Cathodic	Anodic	5
Anodic	Cathodic	10
Cathodic	Anodic	5
Anodic	Cathodic	5

TABLE 2 Pulse setting for power source

Note: The electrodes closest to the samples were polarized as shown. Between polarization shifts, a five-second pause was taken, during which no current was applied to the system and circuitry was manually changed to allow changes to polarization.

TABLE 3 Factor analysis for studied variables

Test run	T (°C)	d_{es} (mm)	U (V)	c (wt%)
1	30	6	30	0.6
2	30	9	30	0.6
3	30	6	40	0.6
4	30	9	40	0.6
5	55	6	30	0.6
6	55	9	30	0.6
7	55	6	40	0.6
8	55	9	40	0.6
9	30	6	30	1.2
10	30	9	30	1.2
11	30	6	40	1.2
12	30	9	40	1.2
13	55	6	30	1.2
14	55	9	30	1.2
15	55	6	40	1.2
16	55	9	40	1.2

from both amperometers for a comparison of current efficiency. The Keysight power source tracked the output current and voltage every 200 milliseconds while the Bahco Multimeter recorded the sample current every 550 milliseconds.

Electrolyte conductivity and temperature were measured with a HACH HQ40D-meter (HACH, USA) using a conductivity sensor (CDC401, 0–200 mS cm⁻¹) before pickling. The ionic concentration of the electrolyte varied between samples, but the effect was small, under 3% of average conductivity of low-level concentration, when compared to increases of 80%–100% caused by the addition of sodium sulfate.

A factorial analysis for temperature, distance between electrode and sample, pickling potential, and electrolyte concentration was conducted using the described system. Sixteen measurements were carried out as presented in Table 3. Two levels for temperature (T), electrode-to-sample distance (d_{es}), potentiostatic cell potential (U), and sodium sulfate concentration (c) were measured. The distance of 6 mm is comparable for the industrial pickling line in relative dimensions. The sodium sulfate concentration of electrolyte solution used in study was significantly lower than the electrolyte concentration used at the industrial pickling plant.^{2,18}

To estimate the factorial effect of each parameter, the results were analyzed using Equation (6), in which the average current efficiency of samples with high parameters (+) are compared to samples with low parameters (–).

$$\text{eff}(x) = \frac{\sum \text{test}(x, +) - \sum \text{test}(x, -)}{8} \quad (6)$$

The effect of the concentration was further evaluated by measuring short, 1-second and 0.5-A galvanostatic pulses with a bipolar system at room temperature (20°C). Annealed and electrochemically pickled 304 stainless steel anodes and grade-1 titanium cathodes were positioned around the sample as shown in Figure 3. Sodium sulfate concentration was studied between 1 and 13 wt%.

3 | RESULTS AND DISCUSSION

Raw data of the measurements are available in the Appendix. Examples of the pickling results can be seen in Figure 4. The end closer to the electrodes had cleaner pickling results, indicating that the current density is not distributed evenly throughout the sample. In addition, the samples with higher average current density were cleaner from oxides.

An example graph from amperometers can be seen in Figure 5. A fast drop in both total current and sample current was observed.

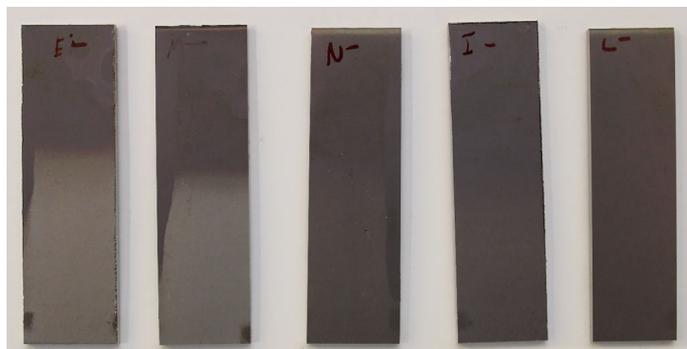


FIGURE 4 Sample pickling results. The samples with high current density had cleaner pickling results, despite lower current efficiency. The dissolution was concentrated to the ends closest to the electrodes

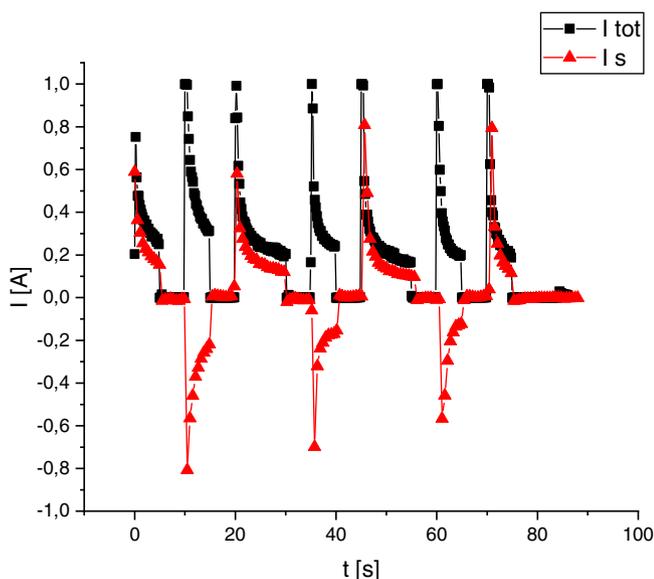


FIGURE 5 Current profiles recorded during pickling reaction. Black line-square is total current applied to system (I_{tot}), while red-triangle is current measured from sample (I_s)

Average total current (I_{tot} , A) was calculated from five first pulse data points of the power source, and average for sample current (I_s , A) was calculated from data points of the multimeter. The current efficiency (I_{eff} , %) was calculated with Equation (7), as the percentage of the total current passing sample.

$$I_{eff} = \frac{I_s}{I_{tot}} \cdot 100\% \quad (7)$$

With these parameters, the average current efficiency was high, on average 67.5%, when compared to the 30% reported by Shapovalov et al¹⁷ and the 20% reported by Ipek et al²⁰. However, current density measured through the sample was somewhat low, being on average 23.5 mA cm^{-2} , with a variation between anodic and cathodic polarization. While over the threshold of gas formation, the current densities reached in this study remain mostly under industrial densities.^{11,13} The average current densities of low and high cell potential differed for 15.3 mA cm^{-2} . The density limits were also recorded with the classical system.

Low current density was caused by high hydrogen overvoltage of titanium electrodes³⁹ and increasing layers of titanium oxide.⁴⁰ This, however, affects the total current and is therefore taken into account when the current efficiency of the system is calculated. Decreasing the current makes, however, a comparison of pickling results impossible, despite being requested by a peer reviewer. The factorial effect of parameters on current efficiency calculated with Equation (1) can be seen in Table 4.

According to a review of microscale bipolar electrochemistry by Fosdick et al,³⁰ the two main mechanisms that affect the electric field formed in bipolar electrochemical systems are cell geometry and conductivity of electrolyte solutions.

The potential applied had a positive effect on both current density and efficiency. Due to passivation lowering both current densities close to the low level, the sample pool for the current density was half of the others and the effect was mixed with that of high temperature. The increase of current density also increases reactions' current efficiency.¹¹ The

TABLE 4 Factorial effect results of studied parameters

	U (V)	i_{average} (mA cm^{-2})	d_{es} (mm)	T ($^{\circ}\text{C}$)	c (wt%)	κ (mS cm^{-1})
I_{Eff} (%)	5.25	6.31 ^a	-2.94	4.36	-7.95 ^b	-7.95 ^b
$I_{\text{Eff}}/\text{unit}$	0.53	0.21 ^a	-0.98	0.17	-14.46	-0.83

^a Effect of current density is calculated from only four sample pairs.

^b These factors will share data.

same effect would explain the increased current passing through the sample, by increasing the reaction kinetics at the bipolar electrode surface. The effect was also recorded by Ipek et al.¹⁷ with bipolar system, but it was not discussed in the results as the focus of study was the effect of insulators. The mechanism of the increase will be the point of interest in our futures studies, as the effect on reaction kinetics was only speculated on by Ipek et al.¹¹

The sample-to-electrode distance lowered pickling efficiency. This is in agreement with results from microreactors²⁶ and experiences from industrial pickling line. Longer distances between samples and electrodes lead to increases in resistance. This increases the current lost to short-circuiting as relative the resistance of competing paths lowers. The distance is, however, limited by the up-and-down movement of the pickling line during industrial process.¹³

Temperature should have a slight negative effect on the current efficiency of the system as it increases the conductivity of electrolytes.^{41,42} The average increase measured was 1.5 mS cm^{-1} . With values for conductivity from Table 4, the decrease in current efficiency should be 1.2%. However, our results disagree, showing increases in efficiency. This suggests that rather than decrease in efficiency by increasing conductivity, the deciding mechanism for temperature is the increase of reaction kinetics reported by Ipek et al.¹¹ The extrapolated difference between pickling efficiency at 70°C and 21°C is 8.3%. This could explain the majority of the reported difference between the 30% of Shapovalov et al.¹³ and the 20% of Ipek et al.¹⁷ Some uncertainty is expected as the studies have other differences in addition to temperature, including unspecified insulation.

In the factorial study, the biggest increase in current efficiency was achieved by decreasing the short circuit current by increasing the resistance of competing paths, that is, decreasing electrolyte concentration. This is the main cause of the high current efficiency of our system. Further evaluation was done utilizing short galvanostatic pulses, as presented in Figure 6, which shows that the effect of concentration is greater at lower concentrations. Between 3 and 13 wt% the increase is rather linear, but it is exponential below 3 wt%. The correlation of linear range is slightly greater to measured conductivity than to wt% of the solution, R^2 of 0.96 versus 0.93, as conductivity does not increase linearly with concentration. Increasing consensus of the neutral electrolytic pickling mechanism is anodic dissolution in which neither sodium nor sulfate participates in reaction. In that case, the conductivity should indeed be more critical than the weight percentage of inert salt chosen for the electrolyte. A comparison of conductivity effect with the model of Ipek et al.¹⁶ is difficult because of a typing error, likely from 10^{-3} to 10^{-6} or 10^{-7} , and the limitations of the model. However, Ipek et al.¹⁶ reported

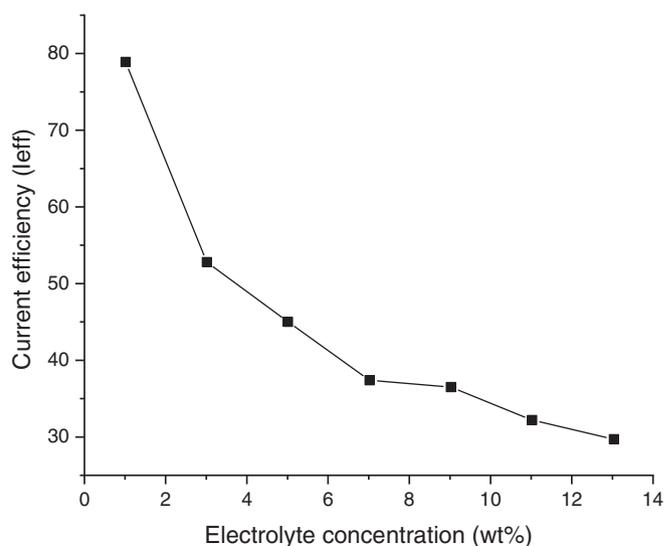


FIGURE 6 The relation between current efficiency and sodium sulfate concentration during galvanostatic current of 0.5 A as measured at room temperature

maximum variation of about 10% in the current efficiency of the system, while our experimental results show a variation of 50%. Of course, due to the error, it is possible that the concentration range values calculated differ significantly from our results.

The electrolyte pH is a point of interest in our future studies, as noted by an anonymous peer reviewer, “of course the pH has an effect,” although we disagree with the simplicity of the effects. The pH can change the reaction conditions in several ways and there remains disagreement between results of Ipek et al.¹¹ and Matsushashi et al.^{3,15} We disagree with the peer reviewer who claimed that conductivity is not deliverable by pH as the pH is a concentration of hydronium ion and conductivity is dependent on ionic concentration of solution. Replacing a portion of sodium sulfate with sulfuric acid is not as straightforward, but according to Lundquist and Lewis,⁴² replacing it decreases conductivity at typical pickling concentrations and temperatures until a fraction of sulfuric acid exceeds 28.6%. Lowering pH increases the solubility of pickling sludge consisting of precipitants of iron, nickel, manganese, and chromium hydroxide.^{12,13,43-45}

For these reasons, future neutral electrolytic pickling research is encouraged to report the conductivity of electrolyte solution used in research, in addition to the combination of pH and dissolved sodium sulfate wt%.

4 | CONCLUSION

In this article, a small, laboratory-scale bipolar pickling device was constructed and used to simulate the industrial electrochemical pickling process. The main observations and contributions of this work are as follows:

- Temperature and cell potential increase the current efficiency of bipolar neutral electrochemical pickling. For temperature, a change of 1°C translates to an increase of 0.17% of current efficiency. For potential, an increase of 1 V translates to an increase of 0.53% current efficiency or 0.34% per increase of 1 mA cm⁻² in average current density. Both temperature and applied potential should remain high to maximize the efficiency of bipolar pickling.
- Cell geometry is a straightforward method to improve pickling effectiveness, but increases are not always possible because of the limitations imposed by industrial systems. Electrodes should be positioned as close as possible to the pickling line.
- Electrolyte concentration decreases current efficiency but decreases cell potential. At low concentrations, the increase of 1 wt% sodium sulfate concentration translates to a decrease of 14% current efficiency, but at concentrations of 3 wt% or more, the decrease is 2.2% per wt% increased. Lower conductivity acts as a natural insulator in bipolar system, decreasing electrode-to-electrode short circuiting.
- Future published results concerning neutral electrochemical pickling should either incorporate bipolar pickling in research or justify the validity of the results to bipolar system in the discussion.

ACKNOWLEDGEMENTS

This research was funded as part of the Business Finland Symbiosis of Metals Production and Nature project (SYMMET). Thanks are expressed to the industrial partners of the project and to Dr. Thomas Ohligschläger for their advice during this research.

PEER REVIEW INFORMATION

Engineering Reports thanks Hong Luo, Sebastian Proch, Tiago F.A. Santos, and other anonymous reviewer(s) for their contribution to the peer review of this work.

PEER REVIEW

The peer review history for this article is available at <https://publons.com/publon/10.1002/eng2.12245>.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTIONS

Teemu Tuovinen contributed to the conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing the original draft, review, and editing. Tuomas Vielma contributed to the supervision, writing the original draft, review, and editing. Ulla Lassi contributed to the funding acquisition, project administration, supervision, writing the original draft, review, and editing.

ORCID

Teemu Tuovinen  <https://orcid.org/0000-0001-6865-0913>

Ulla Lassi  <https://orcid.org/0000-0001-5319-9525>

REFERENCES

1. Sverdrup HU, Olafsdottir AH. Assessing the long-term global sustainability of the production and supply for stainless steel. *Biophys Econ Resour Qual.* 2019;4:8.
2. Laukka A, Heikkinen E-P, Fabritius T. In-depth oxide scale growth analysis of B and Ti microalloyed AISI 304 in oxygen-containing furnace atmospheres and CH₄ burn-simulating furnace atmospheres. *Steel Res Int.* 2019;90:1800447.
3. Li L-F, Celis J-P. Pickling of austenitic stainless steels (a review). *Can Metall Quart.* 2003;42:365-376.
4. Habib KA, Damra MS, Saura JJ, Cervera I, Bellés J. Breakdown and evolution of the protective oxide scales of AISI 304 and AISI 316 stainless steels under high-temperature oxidation. *Int J Corros.* 2011;2011:1-10.
5. Donik Č, Kocijan A, Mandrino D, Paulin I, Jenko M, Pihlar B. Initial oxidation of duplex stainless steel. *Appl Surf Sci.* 2009;255:7056-7061.
6. Lindell D, Pettersson R. Pickling of process-oxidised austenitic stainless steels in HNO₃-HF mixed acid. *Steel Res Int.* 2010;81:542-551.
7. An LC, Cao J, Zhang T, Yang YT. Cr diffusion and continuous repairing behavior during high-temperature oxidation of duplex stainless steel. *Mater Corros.* 2017;68:1116-1122.
8. Cheng S-Y, Kuan S-L, Tsai W-T. Effect of water vapor on annealing scale formation on 316 SS. *Corros Sci.* 2006;48:634-649.
9. Hildén JMK, Virtanen JVA, Ruoppa RLK. Mechanism of electrolytic pickling of stainless steels in a neutral sodium sulphate solution. *Mater Corros.* 2000;51:728-739.
10. Hildén J, Virtanen J, Forsén O, Aromaa J. Electrolytic pickling of stainless steel studied by electrochemical polarisation and DC resistance measurements combined with surface analysis. *Electrochim Acta.* 2001;46:3859-3866.
11. Ipek N, Holm B, Pettersson R, Runnsjö G, Karlsson M. Electrolytic pickling of duplex stainless steel. *Mater Corros.* 2005;56:521-532.
12. Braun E. How to improve pickling of stainless steel strip. *Iron Steel Eng.* 1980;57:79-81.
13. Shapovalov E, Shlyamnev AP, Ul'yanin EA, et al. Investigation of operating parameters of neutral electrochemical pickling bath. *Steel USSR.* 1982;12:215-219.
14. Li L-F, Caenen P, Jiang M-F. Electrolytic pickling of the oxide layer on hot-rolled 304 stainless steel in sodium sulphate. *Corros Sci.* 2008;50:2824-2830.
15. Matsuhashi R, Ito S, Nakata M, Oikawa Y, Ohmura K. The anodic dissolution behavior of oxide films formed on annealed stainless steels in acidic sulfate solution. *Corros Eng.* 1993;42:576-584.
16. Ipek N, Lior N, Bark F, Eklund A, Alemany A. Simple analytical model predicting some features of the electrolytic steel-pickling process. *Russ J Electrochem.* 2002;38:238-246.
17. Ipek N, Lior N, Eklund A. Improvement of the electrolytic metal pickling process by inter-electrode insulation. *Ironmaking Steelmaking.* 2005;32:87-96.
18. Ipek N, Lior N, Vynnycky M, Bark FH. Numerical and experimental study of the effect of gas evolution in electrolytic pickling. *J Appl Electrochem.* 2006;36:1367-1379.
19. Shapovalov E, Kazakova G, Andrushova N. Pickling and passivation processes in Bath of contactless electrochemical pickling. *Steel USSR.* 1983;13:27-31.
20. Ipek N, Cornell A, Vynnycky M. A mathematical model for the electrochemical pickling of steel. *J Electrochem Soc.* 2007;154:P108.
21. Ipek N, Vynnycky M, Cornell A. A coupled electrochemical and hydrodynamical two-phase model for the electrolytic pickling of steel. *J Electrochem Soc.* 2008;155:P33.
22. Vynnycky M, Ipek N. Electrochemical pickling. In: Hegarty A, Kopteva N, O'Riordan E, Stynes M, eds. *BAIL 2008—Boundary and Interior Layers.* Berlin/Heidelberg, Germany: Springer; 2009:287-294.
23. Vynnycky M, Ipek N. Supporting electrolyte asymptotics and the electrochemical pickling of steel. *Proc R Soc A Math Phys Eng Sci.* 2009;465:3771-3797.
24. Vynnycky M, Ipek N. Reaction-layer asymptotics and the electrochemical pickling of steel. *Proc R Soc A Math Phys Eng Sci.* 2011;467:2534-2560.
25. Schmuki P. Electrochemical behavior of Cr₂O₃/Fe₂O₃ artificial passive films studied by in situ XANES. *J Electrochem Soc.* 1998;145:791.
26. Fosdick SE, Knust KN, Scida K, Crooks RM. Bipolar electrochemistry. *Angew Chem Int Ed.* 2013;52:10438-10456.
27. Li X, Lv M, Yin W, Zhao J, Cui Y. Desulfurization thermodynamics experiment of stainless steel pickling sludge. *J Iron Steel Res Int.* 2019;26:519-528.
28. Yang C, Pan J, Zhu D, Guo Z, Li X. Pyrometallurgical recycling of stainless steel pickling sludge: a review. *J Iron Steel Res Int.* 2019;26:547-557.

29. Xie Q, Shi P, Liu C, Jiang M. Effects of different oxidants on HCl-based pickling process of 430 stainless steel. *J Iron Steel Res Int.* 2016;23:778-783.
30. Homjabok W, Permpoon S, Lothongkum G. Pickling behavior of AISI 304 stainless steel in sulfuric and hydrochloric acid solutions. *J Metals Mater Miner.* 2010;20:1-6.
31. Li L-F, Caenen P, Celis J-P. Effect of hydrochloric acid on pickling of hot-rolled 304 stainless steel in iron chloride-based electrolytes. *Corros Sci.* 2008;50:804-810.
32. Narváez L, Cano E, Bastidas JM. Effect of ferric ions in AISI 316L stainless steel pickling using an environmentally-friendly H₂SO₄-HF-H₂O₂ mixture. *Mater Corros.* 2003;54:84-87.
33. Li H, Zhao A. Pickling behavior of duplex stainless steel 2205 in hydrochloric acid solution. *Adv Mater Sci Eng.* 2019;2019:1-6.
34. Li L-F, Caenen P, Daerden M, et al. Mechanism of single and multiple step pickling of 304 stainless steel in acid electrolytes. *Corros Sci.* 2005;47:1307-1324.
35. Negro C, Blanco MA, López-Mateos F, et al. Free acids and chemicals recovery from stainless steel pickling baths. *Sep Sci Technol.* 2001;36:1543-1556.
36. Geng S, Sun J, Guo L. Effect of sandblasting and subsequent acid pickling and passivation on the microstructure and corrosion behavior of 316L stainless steel. *Mater Des.* 2015;88:1-7.
37. Yue Y, Liu C, Asselin E, Shi P, Jiang M. Kinetics of passive film growth on 304 stainless steel in H₂SO₄ pickling solution under chemical oxidation. *Corrosion.* 2018;74:705-714.
38. Ikeda, S.. Technical Progress of Stainless Steel and its Future Trend. *Nippon Steel Technical Report.* 2010;99. <https://www.nipponsteel.com/en/tech/report/nsc/pdf/n9902.pdf>.
39. Stern M, Wissenberg H. The electrochemical behavior and passivity of titanium. *J Electrochem Soc.* 1959;106:755.
40. El-Basiouny MS, Mazhar AA. Electrochemical behavior of passive layers on titanium. *Corrosion.* 1982;38:237-240.
41. Newman JS, Thomas-Alyea KE. Introduction. *Electrochemical Systems.* Hoboken, New Jersey: John Wiley & Sons, Inc.; 2004;1-27.
42. Lundquist RV, Lewis RW. Conductivity of sodium sulfate solutions containing sodium hydroxide or sulfuric acid. *Ind Eng Chem Chem Eng Data Series.* 1957;2:69-72.
43. Stefánsson A. Iron(III) hydrolysis and solubility at 25 °C. *Environ Sci Technol.* 2007;41:6117-6123.
44. Gayer KH, Garrett A. The equilibria of nickel hydroxide, Ni(OH)₂, in solutions of hydrochloric acid and sodium hydroxide at 25. *J Am Chem Soc.* 1949;71:2973-2975.
45. Rai D, Sass BM, Moore DA. Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. *Inorg Chem.* 1987;26:345-349.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Tuovinen T, Vielma T, Lassi U. Laboratory-scale simulation of industrial neutral electrolytic pickling as a bipolar system—Parameters affecting indirect polarization pickling of annealed stainless steel. *Engineering Reports.* 2020;e12245. <https://doi.org/10.1002/eng2.12245>