Hydrochloric Acid Pickling Process Optimization in Metal Wire Working

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***Abstract* — In this paper, the characteristics of metal wire surface scale, acid reaction mechanism, influencing factors and the status quo of pickling process, were proposed. At present, the existing acid pickling process is under low efficiency, and the oxidation iron on the surface of metal wire products cannot be completely removed. In order to enhance the level of metal wire pickling technology and improve the current status, some pickling process optimization schemes were proposed in this paper. The influence factors of pickling process were discussed, including the temperature of hydrochloric acid pickling solution, free HCl concentration, inclusion, environmental temperature, metal wire rod steel grade and acid liquid additives. Besides, the process of the optimized scheme was experimental researched. It can be shown from the experiment that the existing rate of pickling process is increased by more than 15% through the optimized pickling process. It obtains better effect of acid pickling, with the objective environment and economic benefits.**

Keywords - pickling, hydrochloric acid, metal wire, process optimization

I. INTRODUCTION

Pickling process is very important in the production of metal works. Its purpose is to remove the metal wire (hereinafter referred to as: wire rod) surface residual acid corrosion on matrix, increase the carrier to ensure lubrication, improve the quality of the steel wire surface for easy cold deformation[1,2]. Pickling can also remove the harmful impurities (and the oxide film)[3], to ensure that the metal wire surface is smooth and clean[4], so the mould scratches during the process of drawing and cold heading or forming can be reduced[5]. Existing pickling process is primarily focused on fully enclosed tunnel pickling, shallow slot turbulent pickling, push-pull pickling and mechanical descaling at home and abroad[6, 7, 8]. The advantage of these processes is continuous, efficient and automatic. The environment pollution caused by volatilization is light. The craft has a high degree of automation. The surface quality of metal wire is stable through these processes. Besides, it lays a foundation for large-scale continuous deep processing of metal wire products[9,10]. But it also has certain defects. Under the pickling process, factors that affect the process are usually acid liquid concentration, temperature, acid liquid inclusions, pickling additives[11], the structure and thickness of metal wire oxide layer[12], etc. The diameter, composition and carbon content[13] of the metal wire are different. The thickness of the oxide layer is also different. Under continuous pickling operation, there inevitably emerging series of pickling problems due to the improper operation of equipment, technology and personnel, such as the inefficiency of pickling, the increasing of acid mist content, the difficulty of acid regeneration, and so on[14,15]. At present, it has gotten good control in the metal wire materials and the concentration of acid liquid abroad, but there still have some over pickling and owe pickling conditions[16]. Therefore, the improvement research under the existing pickling process has very practical significance[17]. The research improves the existing pickling process from the following aspects, acid liquid concentration, and inclusion concentration in the pickling solution, acid pickling temperature, steel grade, and additives.

II. MATERIALS AND METHODS

A. Test materials and equipment

Materials: concentrated Hydrochloric acid(HCl) (36%) (CP); Metal wire steel grade: Qing-Steel 35#, Qing-steel 45#, Bao-Steel 50#, Sha-Steel 70#, Bao-Steel 82#, 6cm in length, 6mm in diameter.

Additives: $FeCl_2$ (CP), OP-10 (CP), Hexamethylenetetramine (CP), phosphoric acid (CP), sodium salicylate (CP).

Experimental apparatus: electronic analytical balance, water bath magnetic stirrer, a thermometer, a stopwatch, etc.

B. *Pickling solution preparation*

Pickling solution 1: Hydrochloric acid of analytically pure (36%) was made up into pickling solution 1 with HCl content 5%, 10%, 15%, 20%, 22%, 25%.

Pickling solution 2: Hydrochloric acid of analytically pure (36%) was made up into pickling solution 2 with HCl content 6%, 9%, 12%, 15%, 20%, 25%, and FeCl2 content 0g/L, 50g/L, 100g/L, 150g/L, 200g/L, 250g/L.

Pickling solution 3: Hydrochloric acid of analytically pure (36%) was made up into pickling solution 3 with HCl content 25%, 20%, 15%, 10%, 5%.

C. *Mechanism of acid pickling*

After hot rolling, the wire rod surface will form a layer of oxide organization[18,19] commonly known as scale, its main composition includes FeO, Fe_3O_4 and Fe_2O_3 from the inside out. For these scale, rich austenite[20,21] (close to ferrous oxide) only exists in the near surface of the steel plate, the iron outer Fe_3O_4 and Fe_2O_3 is difficult to dissolve in the acid solution. But as a result of cracks and pores that are exist in oxidation layer, acid liquid can reach to the surface of the metal and rich austenite layer through these cracks and porosity. The dissolution of metallic iron and austenite reduce the adhesion between iron and metal, and under the action of hydrogen that generated in the process of acid liquid and metallic iron reaction, the scale become detached from the substrate. At the same time, the undissolving Fe_3O_4 and Fe_2O_3 are revert to easily dissolved FeO, so that the oxide iron falls off from the steel surface. Specific reaction [5] as follows:

(1) Oxide reaction with acid

$FeO+2HCl=FeCl_2+H2O$

$Fe_2O_3+6HCl=2FeCl_3+3H_2O$

(2) Metal reaction with acid

$Fe+2HCl=FeCl_2+H_2$

(3) Reduction reaction of high valent oxide and hydrogen

$Fe_2O_3+2[H]=2FeO+H_2O$

$Fe_3O_4+2[H]=3FeO+H_2O$

$FeCl_3+[H]=FeCl_2+HCl$

The metal reaction with acid to form hydrogen plays a dominant role, followed by oxide iron reaction with acid.

III. RESULTS AND DISCUSSION

A. *Effect of acid liquid concentration on wire pickling*

Take six metal wire roots with a steel grade of 70# which was made from Sha-Steel, record the sample number and weight. Take six beakers, the capacity is 50 ml, with water bath heating in the constant temperature of 30 centigrade and stay for 30 minutes. Each contains pickling solution with a different concentration of 5%, 10%, 15%, 20%, 22%, 25% of HCl. After temperature stabilized, wire samples were included in the pickling solution, respectively, every 20 seconds, wire steel were removed to rinsed, dried, weighed and then record.

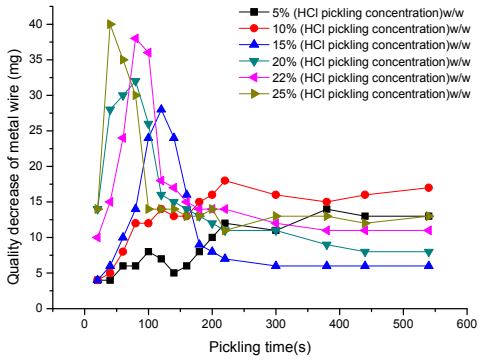

Figure 1. Effect of HCl concentration to 70# Metal wire's pickling

In this study, we could see from figure 1, the higher concentration of HCl pickling solution, gain the greater pickling rate , vice versa. In pickling process, the surface of metal wire has a large number of bubbles, when the concentration raised, the violent reaction became greater, mechanical exfoliation force from hydrogen to oxide skin of metal wire became more stronger. When the concentration of HCl pickling solution between 15%(w/w) and 22%(w/w), acid pickling time within 7 to 10 min, it has been optimum pickling speed. And now wire surface is brightness like before. Especially in a HCl pickling solution concentration of 25%(w/w), acid pickling speed been fastest, reactions violent and surface erosion of wire more easily comes. The same as when the concentration of HCl pickling solution below 15%(w/w), the acid pickling speed turns slower with times decreased, pickling slower easily prone to hydrogen embrittlement and meanwhile energy consumption raised. So there is no suggestions to choose this HCl solution.

B. *Effect of additive amounts of FeCl2 on wire pickling work*

Take six metal wire roots with a steel grade of 70# which was made from Sha-Steel, record the sample number and weight. Take six beakers, the capacity is 50 ml, with water bath heating in the constant temperature of 30℃ and stay for 30 min. Each beaker contains pickling solution with a different concentration of 0g/L,50 g/L,100 g/L,150 g/L,200 g/L,250 g/L(w/v) of HCl. After temperature keep stably and $FeCl_2$ dissolved completely, wire samples were separately immerged into the HCl pickling solution and record the complete pickling cost time. Later we change the concentration of HCl as 9%, 12%, 15%, 20%, 15% (w/w)and repeat the experiments like before.

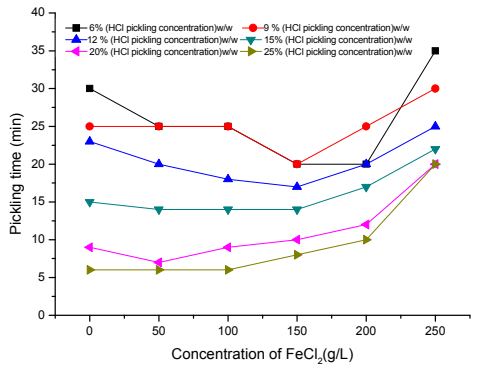

Figure 2. Effect of additive amounts of $FeCl_2$ on wire pickling

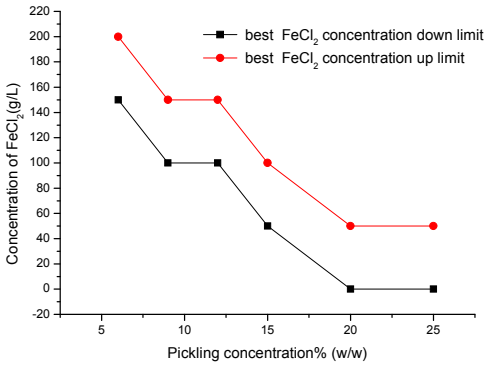

Figure 3. The best concentration range of $FeCl_2$ under different concentration of hydrochloric acid pickling

In this study, we could see from figure 2, When pickling, acid liquid temperature is simulated to 20 □ and control the number of $FeCl_2$ in the acid liquid, The effects of content of $FeCl_2$ in the acid to the pickling rate. It obviously shown that, to get the best pickling rate, should control the concentration of HCl, content of $FeCl_2$ in HCl. The lower the concentration of HCl, the higher content of $FeCl_2$ did the best pickling rate needed, usually content of $FeCl_2$ is less than 250g/L(w/v), when content of $FeCl_2$ in the concentration of HCl is too high and it has been saturated and crystallization which makes pickling efficiency turns lower. We could see from figure 3, mass concentration of $FeCl_2$ in different concentration of HCl pickling solution should between the upper and lower limit level, then it can achieve the optimal rate of pickling.

C. Effect of temperature on wire pickling

Take five roots of metal wire with a steel grade of 70# which was made from Sha-Steel, record the sample number and weight. Take five beakers, equipped with 50 ml of HCl pickling solution which concentration was 5%, put the 5 beaker in water bath heating with a constant temperature, respectively to 10 □, 20 □ and 30 □, 40 □, 50 □. After temperature stability, wire samples were dip into acid lotion and record the complete pickling time separately. Change the concentration of HCl as 25%, 20%, 15% and 10% respectively, repeat the experiments later.

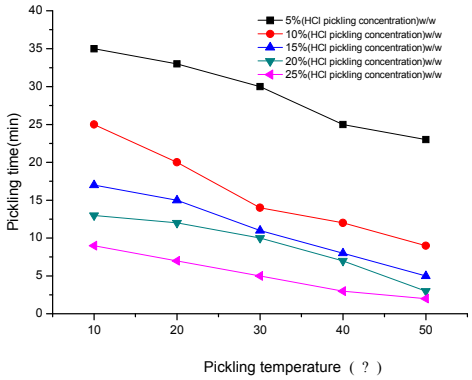

Figure 4. Effect of temperature on wire pickling rate

In this study, we could see from figure 4, When temperature of HCl pickling solution range from 10□ to 50□, pickling speed turn fast with the rise of temperature, quantity of acid mist increased meanwhile, each surface of wire was different. When pickling temperature at range of 10□ to 30□, pickling speed slower gradually, surface of wire turn to a bright yellow color after pickling; we could see from figure 5, when pickling temperature in the range of 30□ to 40□, pickling rate faster than before, surface of the wire appeared to a bright ash color, the texture is smooth, the acid pickling effect is best this time .When acid liquid temperature is upper than 40 □, the pickling rate to speed up the same time a large amount of acid fog produced. So it is recommended to use in air dry condition, with a good ventilation and absorption tower in pickling workshop and a normal air pressure. Furthermore, if weather in low pressure and high temperature conditions in summer, in some areas pickling was forbidden, this because it could easy to cause air pollution and did harm to local person, it also can aggravate the corrosion of equipment.

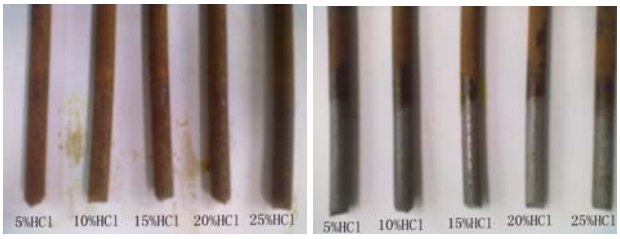

Figure 5. Pictures of wire compared after acid pickling at 30□

D. Effect of HCl pickling additives for wire pickling rate

In this study, in order to study the effect of the dosage of additives on pickling rate, we through a lot of experiments to gain the optimum concentration of each additive adding acid lotion scope is shown in table 1.

TABLE I. OPTIMUM CONCENTRATION SCALE OF PICKLING ADDITIVES

Sample	Reagent	Optimum concentration g/L(w/v)
1	Hexamethylenetetramine	0.8-1.2
2	OP-10	0.5-1.5
3	Phosphoric acid	90-100
4	Sodium salicylate	0.5-1.5

TABLE II. DOSAGE OF ADDITIVE IN PICKLING FORMULA

Formula sample	OP-10	Hexamethylenetetramine	Phosphoric acid	Sodium salicylate
1	0	0	0	0
2	0.05g	0	0	0
3	0.05g	0.05g	0	0
4	0.05g	0.05g	2ml	0
5	0.05g	0.05g	2ml	0.05g

Take five roots of metal wire with a steel grade of 70# which was made from Sha-Steel, record the sample number and weight. Take five beakers, equipped with 50 ml of HCl pickling solution which concentration was 20%, put the 5 beaker in water bath with 30□ constant temperature. After temperature stability, add pickling additive in accordance with table 2. After being acid liquid temperature stability, wire samples respectively to be included in the pickling solution, and record the complete pickling time separately, then repeat the parallel experiments in use of the additives for 5 groups.

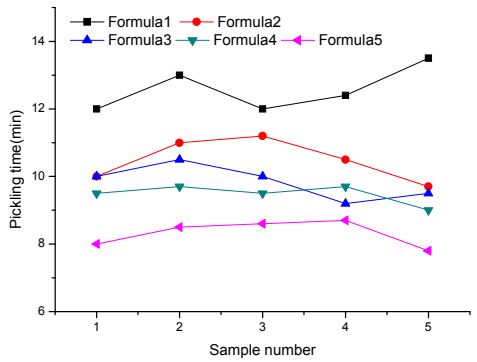

Figure 6. Wire pickling rate under different additives content

In this study, we could see from figure 6 and the actual test phenomenon, when additives is added, it promote the improvement of the pickling rate, and to a certain extent, inhibit the evaporation of acid mist. Compound recipe pickling solution pickling rate is much higher than single recipe or not added to the pickling, OP-10 as surfactants play a leading role in improving pickling rate, when acid wash, it increases the infiltration and wetting of wire surface crack. Accelerate the response of FeO on acid and oxide skin lining. Through certain electrostatic effect, dispersion, stripping scale on the surface of the metal wire to facilitate pickling work, at the same time it promote the acid lotion taking corrosion inhibitor into the surface under subcutaneous oxide of metal. As soon as possible, play a better role of corrosion and produce molecular membrane or bubble formation on the solution surface which inhibit acid mist overflows. In order to improve the rust cleaning effect, a moderate amount of the addition of sodium salicylate can increase the activity of OP-10. For much more addition of Hexamethylenetetramine will cause the corrosion of the metal substrate, acid pickling temperature is too high and together reduce the pickling speed, therefore Hexamethylenetetramine is not for quick cleaning. So add compound additive system. Especially a moderate amount of the addition of phosphate, can complexing iron and accelerate the acid pickling.

E. Effect of different grade of metal on wire pickling

Take five wire roots of different kinds, named 35# and 40#(made from Qing-Steel), 50# and 82#(made from Bao-Steel), 70#(made from Sha-Steel) etc. record the sample number and weight. Take five beakers, equipped with 50 ml of HCl pickling solution which concentration was 20%, put the 5 beaker in water bath with 30□ constant temperature. After about 30min, the temperature stability, put wire roots into pickling bath and record the complete pickling time separately, then repeat experiments as needed.

TABLE III. EFFECT OF QUALITY OF METAL ON AFTER 10 MIN PICKLING

Sample	Qing-Steel 35#	Qing-Steel 45#	Bao-Steel 50#	Sha-Steel 70#	Bao-Steel 82#
Initial quality(g)	29.878	29.948	30.123	27.153	29.876
weight loss(g)	0.163	0.153	0.141	0.114	0.118
weight c rate%	0.54	0.51	0.46	0.42	0.41

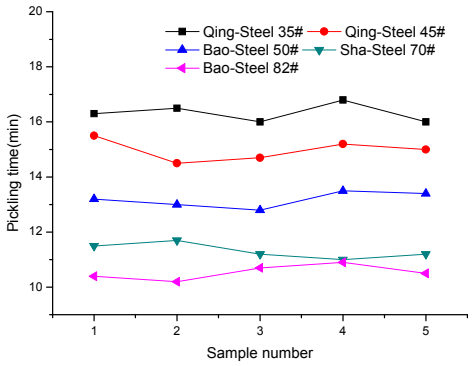

Figure 7. Pickling rate of different grade of metal wire

In this study, we can see form table3, under the condition of same pickling, after 10 min pickling, Acid treatment of metal wire weight loss decreases in turn, from metal wire grade of 35#, 45#, 50#, 70# and80#. This is associated with the thickness of oxide skin that is difference in each steel grade. Metal wire 35# (Qing-Steel) has the most thickness oxide skin, and lead to the longest pickling time and a greater weight loss when pickling. We can also see from figure7, 82#(Sha-Steel)metal wire has a fastest pickling rate, this shows that there is a connection between carbon content

of metal wire and acid pickling rate. When carbon content of metal is increased, and pickling rate will go fast.

IV. CONCLUSION

With the development of iron and steel industry, progress in the pickling directly affects the enterprise's economic toward social benefit. The purpose of this study is based on the optimization of each process parameter in the pickling process and the useful method of acid washing liquid and concentration of additives and control of inclusion, and applied to the actual pickling work, gain the beneficial effect of pickling, improved the existing disadvantages of pickling process. By studying the effects of pickling rate on pickling solution concentration, pickling bath temperature, acid inclusions and the concentration of the pickling additive, the best pickling process parameters and control method is explored. According to the requirements of the metal wire pickling process: it recommend that the use of the acid concentration control between15% to 22%, for the most appropriate pickling time might from 7 to 10 min. Inclusion content should be change towards the HCl concentration in a certain range, usually contents of $FeCl_2$ is less than 250 g/L. Temperature of acid should be controlled between 30□ to 40 □, at the same time affected by environmental factors such as air pressure, workshop ventilation, acid temperature appropriate adjustments is suggested in the summer. Finally different composition formula as pickling additives is studied on the effects of metal wire pickling rate, the optimum additive formula is No.5, it contains 0.05g OP-10 with 0.05gHexamethylenetetramine with 2ml phosphoric acid and 0.05g sodium salicylate.

Therefore additives has a positive effect on accelerating pickling and acid mist inhibition. Application of the optimized pickling process, surface quality of metal wire improved, pickling efficiency improved obviously, and the production of acid mist volatilization and waste acid are both reduced, which has a certain environmental friendliness and played a positive role in the metal wire production process optimization.

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