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# EXPERIMENTAL STUDY ON SOLIDIFICATION/STABILIZATION OF Cr IN STAINLESS STEEL PICKLING SLUDGE BY HIGH TEMPERATURE ROASTING PROCESS

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For stainless steel pickling sludge (SSPS) produced in a stainless steel factory in southeast China, Fly ash (FA) and waste glass (WG) were used as solidification/stabilization (S/S) agents to conduct high-temperature roasting experiments on S/S of Cr in SSPS, respectively. The effects of roasting temperature and S/S agent dosage on the S/S of Cr were studied. The results show that both FA and WG can take positive way to S/S. By adding 25 % of FA to SSPS at roasting temperature of 1 500 °C, the Cr leaching concentration of S/S products can decrease to 0,63 ppm. As for WG as S/S agent, the Cr leaching concentration of the product can be reduced to 0,45ppm when the dosage is 20 % and the roasting temperature is 1 400 °C,. Considering the dosage and roasting temperature, WG is suggested as a better S/S agent.

*Keywords:* stainless steel Cr, solidification, pickling sludge, temperature, roasting

## INTRODUCTION

Stainless steel is widely used in construction, biomedicine, food and other industry and life fields because of its excellent rust and corrosion resistances [1]. At the same time, stainless steel production process can produce a large number of SSPS, with an output basically equal to 3 ~ 5 % of stainless steel production [2]. Global crude stainless steel production reached 58,289 million metric tons in 2021, 14,5 % higher year on year, according to 2021 annual stainless steel production sheet by the International Stainless Steel Forum's (ISSF). Among them, China's annual production of stainless steel in 2021 was 32,632 million metric tons, with a year-on-year increase of 5,1 % [3]. Deduced from the statistics above, the production of SSPS in China of 2021 is approximately 0,98 ~ 1,63 million metric tons. SSPS contains $Cr^{6+}$, which does great harm to the ecological environment for a long time. $Cr^{6+}$ has strong mobility and strong solubility, and can exist in five forms of $H_2CrO_4$, $HCrO_4^-$, $CrO_4^{2-}$, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ in aqueous solution [4]. $Cr^{6+}$ can be easily absorbed by human body through digestive tract, respiratory tract, skin and mucous membrane. It is a highly toxic carcinogenic substance, which is extremely harmful to human health. It has been included in the hazardous waste for strict management and disposal in China.

In annealing, normalizing, quenching, normalizing and other stainless steel processes, iron sheet will be generated on stainless steel surface, of which the main components are FeO, $Fe_2O_3$, $NiO_2$, $Cr_2O_3$, $Fe_3O_4$, $FeO·Cr_2O_3$, $Ni·Fe_2O_3$, $FeO·Cr_2O_3·Fe_2O_3$ and other compact oxides. The basic adhesion of these oxides is strong. After shot blasting, high temperature alkali etching, molten salt electrolysis, mixed acid washing, multistage rinsing and other combined processes, stainless steel pickling wastewater will be produced. After neutralization and precipitation, sludge concentration and dehydration, SSPS is formed [5]. The chemical compositions of several typical SSPS are shown in Table 1, from which it can be seen that the SSPS obtained by different pickling processes in different plants differ greatly in chemical compositions. But they mostly contain elements such as Cr, Ni, Fe, Ca, F, S, and Si. The heavy metal oxides of Cr generally account for more than 5 % of the composition of sludge, which may cause serious pollution problems if not properly disposed.

As mentioned above, the huge production capacity and great harmfulness make the harmless treatment of pickling sludge in stainless steel plants and it has become the focus of research on environmental governance in steel mills, and some achievements have been made by researchers. The methods for SSPS disposal are mainly divided into two categories: harmless treatment and S/S treatment. In the harmless treatment, the $Cr^{6+}$ in the SSPS is generally reduced to $Cr^{3+}$ by reduction reaction, including high temperature reduction [6], wet reduction [7] and biological reduction [8]. The S/S treatment is widely acknowledged as an important method to dispose the SSPS. This method is to solidify or stabilize Cr in some materials so that it can stably exist in the material and become difficult to dissolve.

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Table 1 **Main chemical compositions of several typical SSPS / wt.%**

| Sample | $Cr_2O_3$ | NiO | $Fe_2O_3$ | CaO | $CaF_2$ | $CaSO_4$ | $SiO_2$ | MgO | MnO | $MoO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 11,5 | 3,0 | 25,8 | 7,3 | 47,5 | 3,0 | 1,8 | 0,7 | - | 0,3 |
| 2 | 6,0 | 3,4 | 28,0 | 11,0 | 51,0 | 0,5 | 1,9 | 0,5 | - | 0,3 |
| 3 | 7,1 | 3,1 | 31,0 | 5,5 | 34,0 | 11,4 | 2,49 | 0,73 | - | 0,61 |
| 4 | 5,07 | 3,18 | 17,5 | 7,95 | 42,7 | 8,50 | 1,15 | 0,92 | 0,45 | 0,24 |

Table 2 **Main chemical compositions of SSPS in this study / wt.%**

| $Al_2O_3$ | CaO | $SiO_2$ | $Fe_2O_3$ | MgO | $Na_2O$ | NiO | F | $Cr_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| 1,1 | 26,5 | 4,35 | 41,4 | 0,15 | 0,37 | 9,68 | 7,39 | 5,41 |

Table 3 **Main chemical compositions of FA / wt.%**

| $Al_2O_3$ | CaO | $SiO_2$ | $Fe_2O_3$ | $TiO_2$ | MgO | $P_2O_5$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|
| 27,26 | 2,20 | 58,71 | 5,81 | 2,47 | 0,74 | 0,53 | 0,32 | 0,92 |

The S/S treatment methods mainly contain conventional material S/S method, roasting S/S method and pharmaceutical S/S method.

In this study, different amounts of FA and WG were used as S/S agents for S/S treatment of the SSPS produced by a stainless steel plant in southeast China. The S/S effects of the two agents on Cr in SSPS were compared.

## MATERIALS AND METHODS

The SSPS used in this study was obtained from a steel plant in southeast China with a moisture content of 71,3 %. It was heated to 105 °C in an oven and held until the weight was constant, and then sampled for X-ray fluorescence (XRF) analysis and X-ray diffraction (XRD) analysis to examine its chemical composition and main crystal phases. Table 2 shows the chemical composition of SSPS obtained by XRF. It shows that the SSPS used in this study mainly contains Ca, Si, Fe, Ni, Cr, F and other elements. The XRD analysis results of the SSPS are shown in Figure 1. According to Figure 1, the main crystalline phase of the SSPS is fluorite, and other components exist in amorphous phase.

The XRF and XRD analysis results of the FA used in this study are shown in Table 3 and Figure 2, respectively. It can be seen from the analysis results that the main component of the FA is silicon and aluminum oxides, while the main crystal phase is silicon dioxide, and the rest of the components exist in amorphous phase.

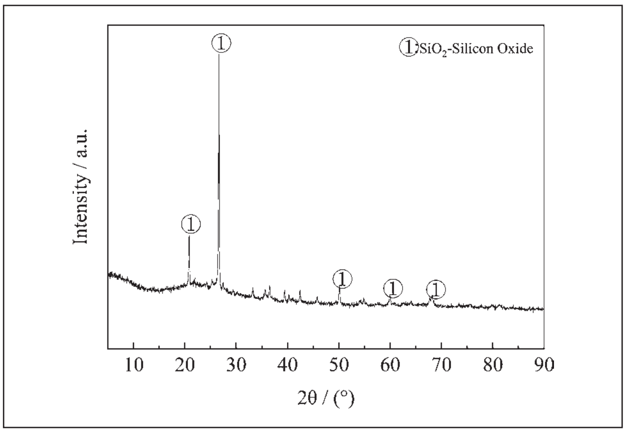


**Figure 2** XRD pattern of FA.

Table 4 **Main chemical compositions of WG / wt.%**

| $Al_2O_3$ | CaO | $SiO_2$ | $Fe_2O_3$ | MgO | $Na_2O$ |
|---|---|---|---|---|---|
| 5,65 | 10,39 | 67,62 | 0,07 | 4,09 | 9,46 |

The XRF and XRD analysis results of the other S/S agent WG are shown in Table 4 and Figure 3, respectively. The results show that the main component of the WG is silicon oxide, with a small amount of oxides containing Na, Ca, Al, Mg and other elements, all of which exist in amorphous phase.

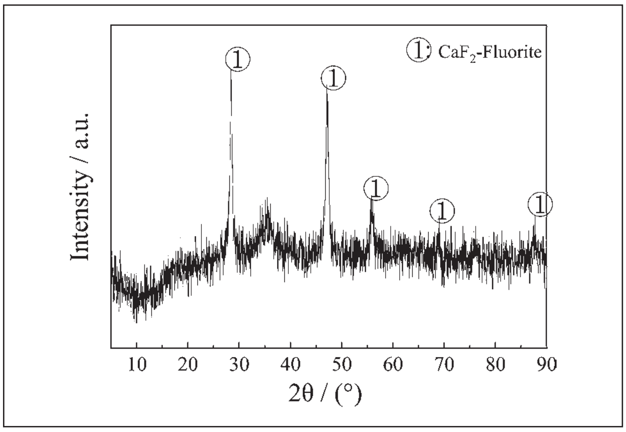


**Figure 1** XRD pattern of SPSS.

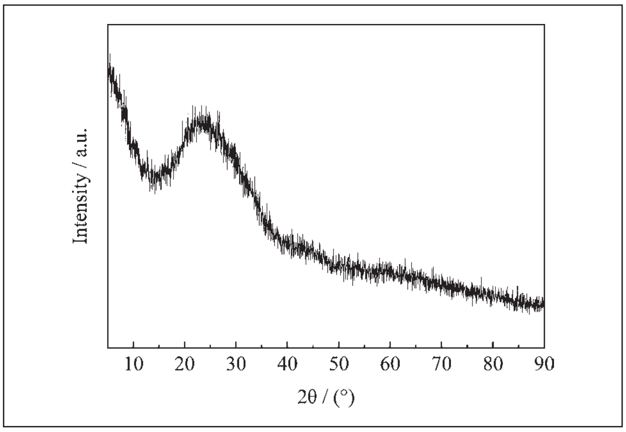


**Figure 3** XRD pattern of WG.

In this study, the optimal roasting temperature and S/S agent dosage were determined for FA and WG. In the first step, two S/S agents taking 20% of the total mass of the mixed material, were used to mix with the SSPS after drying, and then the mixed materials were heated to 900 °C, 1 000 °C, 1 100 °C, 1 200 °C, 1 300 °C, 1 400 °C, 1 500 °C and 1 600 °C for one hour in a Muffle furnace to conduct the S/S temperature tests, respectively. The leaching concentration of Cr in the tested products was detected by ICP to determine the appropriate S/S temperature. In the second step, the S/S agent dosage test was carried out with the S/S agent occupying 15 %, 20 %, 25 %, 30 % of the total mass of the mixed materials under the appropriate S/S temperature, to determine the optimal S/S agent dosage. Finally, the S/S agent was chosen with its optimal S/S conditions.

## RESULTS AND DISCUSSION

The results of temperature test using FA and WG are shown in Figure 4. When FA was used as S/S agent, the leaching concentration of Cr decreased obviously with the increase of roasting and S/S temperature. From 900 °C to 1 500 °C, the leaching concentration of Cr in the S/S products decreased gradually from 6,47 ppm to 0,84 ppm. The leaching concentration of Cr in the product after S/S at 1 600 °C was 0,79 ppm. The results show that the high temperature roasting and S/S process of SSPS with FA as S/S agent is very effective. Considering the heating cost and S/S effect at different temperatures, 1 500 °C was chosen as the optimum temperature for the test of high temperature roasting and S/S of SSPS with FA. When WG was used as S/S agent, from 900 °C to 1 600 °C with 100 °C in interval, the leaching concentration of Cr is 4,89 ppm, 3,52 ppm, 2,59 ppm, 1,83 ppm, 1,06 ppm, 0,46 ppm, 0,43 ppm, 0,41 ppm, respectively. It can be seen that the S/S effect of WG as S/S agent for Cr in SSPS is better than that of FA. When the temperature reached 1 400 °C, increasing the roasting temperature would not improve the S/S effect. Therefore, 1 400 °C was chosen as the optimal roasting and S/S temperature for the S/S agent of WG.

The results of dosage test using FA and WG are shown in Figure 5. When FA is used as the S/S agent, the leaching concentration of Cr detected from the four leaching solutions with 15 %, 20 %, 25 %, 30 % proportions of S/S agent are 1,34 ppm, 0,87 ppm, 0,63 ppm and 0,59 ppm, respectively. It can be seen that increasing the amount of FA as the S/S agent can reduce the leaching concentration of Cr in the roasting and S/S products of SSPS. Furthermore, with the increase of FA mass proportion, the decrease trend of leaching concentration of Cr gradually slowed down. When the amount of FA reaches 25 %, it was of little significance to increase the amount to improve the S/S effect, so 25 % was chosen as the best dosage of FA. When WG was used as S/S agent, the leaching concentration of Cr of 4 S/S products in 15%, 20%, 25%, 30% of S/S agent were 0,74 ppm, 0,45 ppm, 0,37 ppm and 0,33 ppm, respectively. Similar to FA, when the dosage increases, the leaching concentration of Cr will further decrease. However, compared with FA, WG as S/S agent has a stronger effect on reducing the leaching concentration of Cr in roasting and S/S products. When the dosage changed from 20 % to 25 %, the leaching concentration of Cr of the FA group still decreased significantly, while the change of the WG group had slowed down. Under same dosage, the leaching concentration of Cr of the WG group was lower than that of the FA group, and the

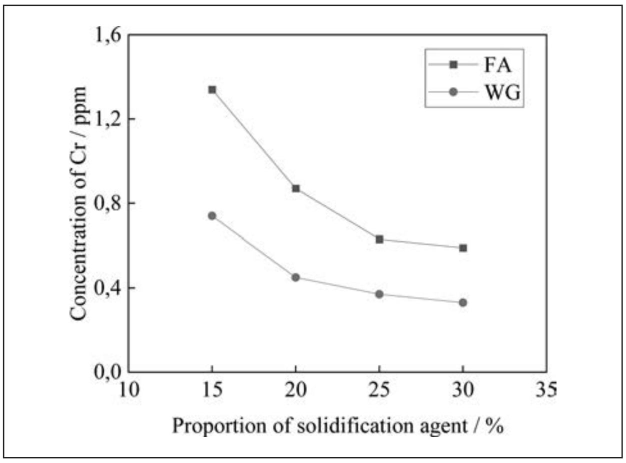


**Figure 5** Dosage test results

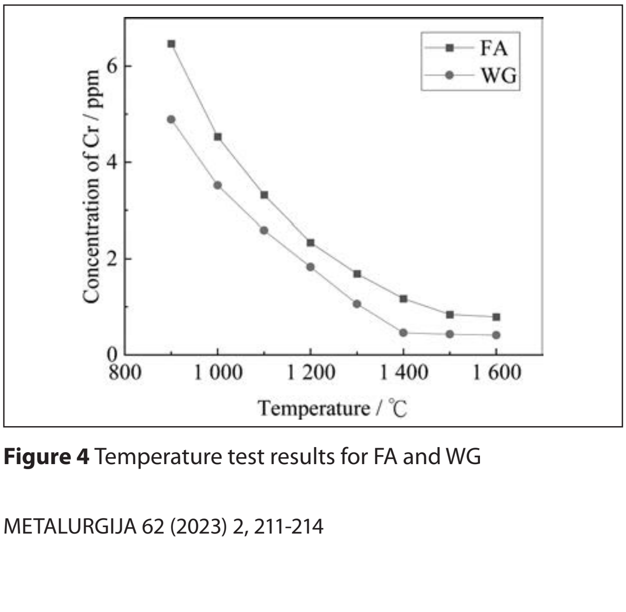


**Figure 4** Temperature test results for FA and WG

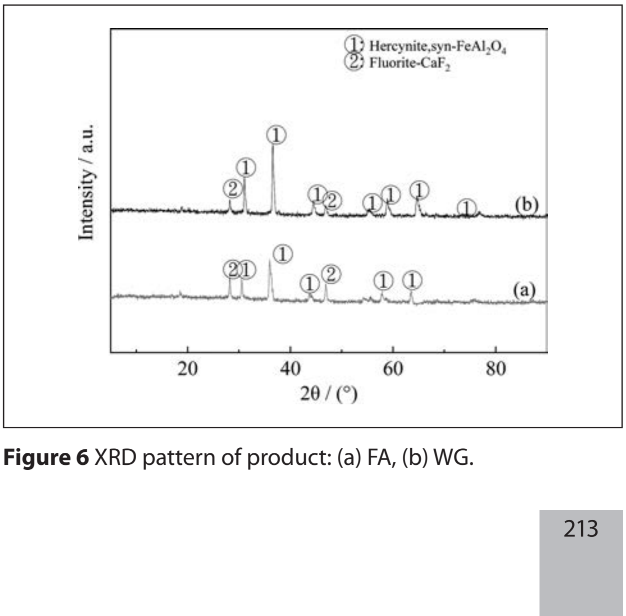


**Figure 6** XRD pattern of product: (a) FA, (b) WG.

roasting temperature of the WG group was lower. It can be seen that WG is better than FA as S/S agent in high temperature roasting for the S/S of Cr in SSPS.

XRD analysis was carried out on the S/S products with FA (dosage: 25 %) and WG (dosage: 20 %). The results are shown in Figure 6. By comparing the XRD patterns of SSPS, it can be seen that after adding two kinds of S/S agents for roasting at high temperature, a large amount of Fe-Al spinel phase was produced in the S/S products, while the amorphous phase originally existed in FA and WG basically disappeared.

## CONCLUSIONS

In this paper, S/S of Cr in SSPS from a steel plant in southeast China by high temperature roasting was studied. By changing the roasting temperature, the dosage and type of S/S agent with high temperature roasting method for the S/S of Cr in SSPS, leaching concentration of Cr and XRD were analyzed on the S/S products. The study reached the following conclusions:

(1) The experiments on the high-temperature roasting and S/S of Cr in SSPS with FA show that FA is an effective S/S agent. The appropriate S/S temperature is 1 500 °C, and the effect is better when the FA content is 25 %. The leaching concentration of Cr in the S/S product is 0,63 ppm, and the effect is not obvious when the addition amount is 30 %.

(2) WG is also a kind of effective S/S agent, and the effect is better than FA. The proper S/S temperature is 1 400 °C. The addition amount of 20 % of WG can achieve good S/S effect, and the leaching concentration of Cr of 0,45 ppm in S/S product. Compared with FA, the optimal dosage and S/S temperature of WG are lower, and the S/S effect is obviously better than FA. Therefore, WG is a better S/S agent than FA.

(3) XRD analysis results show that whether FA or WG is used as S/S agent, a large amount of Fe-Al spinel phase is produced in the products of S/S, so it is speculated that Fe-Al spinel has a better S/S effect than Cr, but further research is still needed to verify.

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**Note:** Wenxiang Deng is the responsible for English language, Beijing, China.