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Chemical fixation of toxic metals in stainless steel pickling residue by $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ and phosphoric acid for beneficial uses

Peidong Su*, Junke Zhang, Yadong Li

Department of Civil & Environmental Engineering, Jackson State University, Jackson, MS, 39217, USA

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ABSTRACT

The leaching concentrations of different metals in stainless steel pickling residue (SSPR) were determined and the toxic metals were treated using $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, and phosphoric acid. A modified European Community Bureau of Reference (BCR) sequential extraction was used to identify the speciation of the concerned metals. Results showed that SSPR contains a large amount of Ca (58.41%), Fe (29.44%), Cr (3.83%), Ni (2.94%), Mn (2.82%) and some of Al, Cu, Mg, Zn. Among them, Cr and Ni were the most toxic metals in SSPR, thus the raw SSPR falls into hazardous waste category due to the leaching amount of Cr. In addition, the leached Cr was identified as Cr^{6+} (MgCrO_4) in the waste. BCR test revealed that risk assessment code (RAC) of Cr and Ni were 33.29% and 61.7%, indicating they posed “high” and “very high” risk to the environment, respectively. After fixing by $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, the leaching concentrations of Cr and Ni were less than 1.5 and 0.5 mg/L, respectively. After fixing by $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ the treated SSPR can be safely reused as roadbed materials, concrete and cement aggregates. This study provides a useful implication in treatment and beneficial reuse of heavy metal-containing hazardous wastes.

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Introduction

Stainless steel consists of a group of metals with high percentage of iron (Fe), chromium (Cr), nickel (Ni) and manganese (Mn). The stainless steel is famous for its corrosion resistance which mainly depends on the amount of Cr. According to the International Stainless Steel Forum (ISSF), the minimum content of Cr in crude stainless steel should no less than 10% (ISSF, 2012). During stainless steel production, pickling is an important process that usually employed to improve the surface quality of the stainless steel. In pickling process,

aggressive mixed acids (i.e., nitric acid and hydrofluoric acid) were used to remove the scale layers from the steel surface and thus, pig iron powder as well as various heavy metals dissolved into pickling liquors (Shi, 2015). The resulted pickling liquors were then precipitated using lime (CaO) or calcium hydroxide ($\text{Ca}(\text{OH})_2$) and produced a large amount of sludge. The sludge was then dewatered and finally converted to residue with a moisture content of 50%–60%. The toxicity characteristic of the residue exceeded the national hazardous waste standards due to the leaching concentrations of Cr and Ni (Zhanget al., 2015; Su et al., 2019a). However, the disposal of stainless steel pickling residue (SSPR) in the hazardous waste

* Corresponding author.

E-mail address: spd1194042797@gmail.com (P. Su).

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landfill is inexecutable due to the high disposal cost and limited landfill space. Therefore, the SSPR had to be temporarily stored on sites in China (NBS, 2013). This provisional solution has the potential of contaminating the sites with heavy metals that could leach out from the SSPR through contacting with rain and surface water. Based on above concerns, there is an acute need to treat and dispose of SSPR.

As have been reported in previous publications, stabilization/solidification (S/S) was commonly used to treat heavy metal-containing solid wastes (Karayannis et al., 2017). Portland cement, fly ash, lime, and thermoplastic materials were widely used as binders (Hu, 2005; Li et al., 2011; Bie et al., 2016). In the S/S process, the mobility of the heavy metals was minimized and the engineering properties of wastes were improved (Wang et al., 2018; Su et al., 2019b). Nevertheless, S/S with above-mentioned binders introduce a large amount of binder that results in a significant increase in the volume and weight of the wastes. This is unacceptable due to the rapid urbanization and increase in the land price. Research indicated that thermal treatment (i.e., incineration, melting and combustion) was an attractive option for waste sludge treatment due to its energy recovery and advantage of reduction of solid waste amount by weight and volume (Zhang et al., 2008; Hu et al., 2013). However, this SSPR was produced from chemical precipitation of industrial pickling liquor that there were almost no organic matters in it. Consequently, SSPR cannot be treated by thermal treatment solely. In this case, Zhang et al. (2017) investigated co-combustion of bituminous coal and pickling sludge in a drop-tube furnace. Their results revealed that heavy metals in flue gas met the national standard, however, the leaching toxicity of the bottom ash exceeded the thresholds for landfill disposal. In addition, harmful off-gases such as SO_2 , NO_x , HF and HCl were detected in the emissions (Zhang et al., 2016).

By comparison, chemical fixation enables to immobilize heavy metals in solid wastes without pre-treatment which makes it cost-efficient, land-saving and thus a promising technology (Jiang et al., 2004; Quina et al., 2014; Wang et al., 2015). Hu (2005) studied the fixation of Pb in municipal solid waste incineration (MSWI) ash using ferrous/ferric solution and stated that when MSWI ash was treated with 1.6 mol/L ferrous/ferric sulfate solution, the formation of MFe_2O_4 and $\text{Ca}_3\text{Fe}_9\text{O}_{17}$ could reduce the leaching concentration of Pb significantly. Moreover, it has been proved that metals in air pollution control (APC) residue could be effectively fixed by soluble phosphates and sodium carbonate (Quina et al., 2010). If the toxic metals in the SSPR can be fixed by chemical fixation, it will provide a new approach to deal with the final disposal of SSPR. Therefore, the objective of this paper was to study the chemical fixation of toxic metals in SSPR. Three chemicals: sodium sulfide hydrate ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$), and phosphoric acid (H_3PO_4) were employed to disclose whether precipitation or reduction working on the treatment of metals in SSPR. The leaching amount of different metals was determined using different toxicity characteristic leaching procedures. A modified European Community Bureau of Reference (BCR) sequential leaching method was conducted to recognize the environmental risk and existing forms of metals in the samples before and after fixation.

1. Materials and methods

1.1. Materials

The SSPR was obtained from Dainan town in Jiangsu province, China. There are over 1200 stainless steel factories in Dainan and thus, the environmental problems caused by SSPR are very prominent in this town. The moisture content of the SSPR was determined to be 53.3% and the pH was measured to be 9.01 according to U.S. Environmental protection agency (EPA) Method 9045D - Soil and waste pH (USEPA, 2004). Before use, the SSPR was dried at 105°C and crushed into fine particles.

The sodium sulfide hydrate ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$) was purchased from Acros Organics, Inc. with the content of pure sodium sulfide of 40.8%. Analytical-grade phosphoric acid (H_3PO_4 , $\geq 85\%$ solution in water), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), trace metal-grade sulfuric acid, nitric acid, hydrochloric acid, HPLC-grade acetic acid, hydrogen peroxide (30% in water), sodium hydroxide beads and other reagents were purchased from Fisher Scientific Co., Ltd in USA without further purification. All the solutions used in this study were prepared by deionized (DI) water.

1.2. Determination of total amount of metals in the SSPR

To evaluate the total amount of the different metals in the SSPR, a two-step digestion process was performed based on USEPA method 3050B - Acid Digestion of Sediments, Sludges, and Soils (USEPA, 1996). This method involves a HNO_3 and H_2O_2 digestion that will dissolve almost all elements that could become environmentally available. For HNO_3 digestion, an aliquot of 1 g SSPR (dry weight) is transferred to a 100 mL beaker, add 10 mL of 1:1 (g/mL) HNO_3 and then, mix the slurry homogeneously and cover the beaker with a glass top. The sample is then heated to $(90 \pm 5)^\circ\text{C}$ and reflux for 15 min. After that, add 5 mL concentrated HNO_3 , replace the cover and reflux for 30 min. If brown fumes are given off, indicating the acid digestion is incomplete. Repeat addition of 5 mL concentrated HNO_3 until no brown fume is generated. Continue heating the sample until the volume has been reduced to about 5 mL. Cool down the HNO_3 -digested sample and carefully add 2 mL of DI water and 3 mL of H_2O_2 to start H_2O_2 digestion. Return the sample to the heater until effervescence subsides. Repeat addition of 1 mL aliquots of H_2O_2 with warming until no obvious effervescence generated. The total addition of H_2O_2 should no more than 10 mL. The sample is then heated to $(90 \pm 5)^\circ\text{C}$ to reduce the volume to about 5 mL. After cooling, dilute the HNO_3 - H_2O_2 -digested sample to 100 mL DI water and re-suspend the sample manually. Separate the residue in the sample and stored at 4°C for analysis.

1.3. Toxicity extraction test

The batch extraction test of SSPR was performed through three different extraction procedures: (1) HJ/T 299-sulphuric acid and nitric acid extraction, (2) HJ/T 300-acetic acid buffer solution extraction, and (3) GB 5086.1-water extraction. Among them, sulphuric acid and nitric acid extraction was used to identify whether or not a waste is hazardous with

Table 1 – Methods and parameters of the leaching test.

Item	HJ/T 299	HJ/T 300	GB 5086.1
Extraction fluid	Dilute H_2SO_4 : $\text{HNO}_3 = 2:1$ (W/W) into 1 L deionized water (1–2 drops)	Add 17.25 mL glacial acetic acid into 1 L DI water	DI water
Solid to liquid ratio (g/mL)	1:10	1:20	1:10
pH of extraction fluid	3.20 ± 0.05	2.64 ± 0.05	8.9
Solid weight (g)	100	75	70
Rotation frequency (r/min)	30 ± 2	30 ± 2	30 ± 2
Extraction duration (hr)	18 ± 0.5	18 ± 0.5	18 ± 0.5
Temperature ($^{\circ}\text{C}$)	23 ± 2	23 ± 2	23 ± 2

respect to its leaching toxicity. Acetic acid buffer solution extraction was designed to simulate the worst-case for pollution control on the sanitary landfill site of solid waste. Water extraction is applicable to the environmental impact assessment of hazardous waste storage and disposal facilities. The extraction fluids and specific parameters of the three methods were presented in Table 1. The detail procedures of the three methods were in accord with our former study (Su et al., 2019c). After extraction, the slurry was filtered through 0.6–0.8 μm glass fiber filter and the filtrate was acidified by concentric nitric acid to $\text{pH} < 2.0$ for storage and further analysis.

1.4. BCR sequential extraction test

As it is well known that the mobility and bioavailability of metals depend significantly on their specific existing forms, the potential hazards of toxic metals rely on their ability to release into the environment (Sungur et al., 2015). The total amount of metals in a solid waste cannot properly express the potential risks of metals to the environment because only a few proportions of the total content will leach out from the solid matrix. Hence, a modified BCR sequential extraction method was applied in this study to estimate the phase associations of samples before and after fixation. The procedures were briefly described in the following.

Step 1. Add 40 mL of DI water to 1 g dried sample in a 50 mL centrifuge tube. Extract for a period of 16 hr using a rotary agitation extractor at (30 ± 2) r/min. Filter the slurry through 0.6–0.8 μm glass-fiber filter and decant the supernatant for analysis. The supernatant is named as water-soluble fraction (F0). Carefully collect the residue and use for step 2 extraction.

Step 2. Add 40 mL of 0.11 mol/L glacial acetic acid to the residue from step 1 and re-suspend the sample. Afterwards, extract for 16 hr using the rotary agitation extractor above. Separate the supernatant as described in step 1. The obtained supernatant is named as acid-soluble fraction (F1).

Step 3. Add 40 mL of 0.5 mol/L $\text{NH}_2\text{OH}-\text{HCl}$ (adjust pH to 1.5 using 1 mol/L HNO_3) to the residue from step 2. Re-suspend the mixture and extract for 16 hr at (30 ± 2) r/min. Separate the supernatant and named as Fe–Mn oxides fraction (F2).

Step 4. Add a total amount of 20 mL of H_2O_2 (30% in water) in 5 mL aliquots, digest the residue from step 3 at 85°C , for a

period of 2 hr in a water bath. Reduce the volume of the mixture by heating till no liquid is observed. Cool down the sample and then extract using 40 mL 1 mol/L $\text{CH}_3\text{COONH}_4$ for 16 hr at (30 ± 2) r/min. Filter the supernatant and named as organic compounds/sulfides fraction (F3).

Step 5. Digest the residue from step 4 in 10 mL aqua regia at 50°C for 16 hr. Then re-suspend the sample by adding 10 mL of 1 mol/L HNO_3 . Separate the supernatant and named as residual fraction (F4).

Among the five fractions, F0 and F1 pose higher risk potential as they are not stable and prone to leach out due to the change of pH. The higher the proportions of a metal in F0 and F1, the greater its leaching potential will be. In contrast, metals existed in F4 was expected due to the high stability and immobility.

1.5. Chemical fixation process

In order to fix the toxic metals in SSPR, $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, and phosphoric acid were used in this study. The dosage of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ varied from 2% to 5% and the dosage of $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ varied from 3% to 10% on the mass basis of oven-dried SSPR. For H_3PO_4 fixation process, phosphoric acid with a mass fraction of 4%–10% was used. Both $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ were dissolved in DI water prior to mixing thoroughly with SSPR with the liquid-to-solid ratio at 1:1 (mL/g) and all the samples were cured in the open air at room temperature ($23 \pm 2^{\circ}\text{C}$). Afterwards, the amounts of the sample as required for extraction tests were taken and dried at 105°C for 24 hr. The dried products were then crushed into fine particles before extraction. The extracts generated from the extraction tests were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (ICPE-9000, Shimadzu, Japan) for the amount (mg/L) of different metals.

1.6. X-ray diffraction and scanning electron microscope analysis

The mineralogy of crystalline phases of the samples was recorded by X-ray diffractometer (XRD) (MiniFlex600, Rigaku, Japan) with Cu anode at 40 kV and 15 mA. The scanning degrees ranged from 10° to 80° by a step width of 0.2° with $2^{\circ}/\text{min}$ speed duration. The micro-morphology of samples was obtained by scanning electron microscopy (SEM) (LYRA3, TESCAN, The Czech Republic).

2. Results and discussion

2.1. Total amount of different metals detected in the SSPR

The total amount of different metals in the SSPR was determined and the results indicated that SSPR contains a large amount of Ca and Fe (175,000 and 88,200 mg/kg, respectively). This is reasonable because $\text{Ca}(\text{OH})_2$ was used to precipitate the pickling liquors and pig iron existed in the scale layer dissolved in the pickling process (Leonzio, 2016). The total amount of other metals followed the order of Cr (11,500 mg/kg) > Ni (8800 mg/kg) > Mn (8470 mg/kg) > Mg (3590 mg/kg) > Al (3150 mg/kg) > Cu (535 mg/kg) > Zn (324 mg/kg). Obviously, the amount of Cr and Ni in the SSPR were relatively high. According to ISSF, Cr in stainless steel is primarily responsible for the self-passivation and corrosion resistance, and stainless steel must have a minimum content of 10.5% of Cr by weight. Besides, Ni was used as an alloying element to improve the corrosion resistance. During pickling process, the scale layer which contains Cr, Ni, Mn, and other metals will be dissolved in the pickling liquors and eventually, these metals were precipitated in the SSPR through neutralization process.

2.2. Extraction test of the SSPR

The concentrations of metals in sulphuric acid and nitric acid extraction, acetic acid buffer solution extraction and water extraction tests are given in Table 2. The related limit for hazardous waste identification in GB 5085.3–2007, standard for entering sanitary landfill in GB16889–2008 and standard for entering hazardous waste landfill in GB18598–2001 were also listed in the table. The leaching concentrations of metals in sulphuric acid and nitric acid extraction test showed that the most remarkable element was Cr with a concentration of 15.2 mg/L. As a result, SSPR fell into hazardous waste. Al and Zn were not detected in the sulphuric acid and nitric acid extraction and the other metals did not exceed the specified thresholds. The results of acetic acid buffer solution extraction revealed that Ca was the dominant element in the extract with a concentration of 2320 mg/L. It was worth noting that Cr and Ni were 193.8 and 202.5 mg/L, which were more than 43-

and 405-times the limits (4.5 and 0.5 mg/L) for entering sanitary landfill. Al, Fe, Mg, and Mn were not notably because they do not pose a threat to the environment. In water extraction test, only Ca, Cr and Mg were detected in the extract and all of them did not exceed the thresholds for entering hazardous waste landfill. Since the unit price of wastes disposed of in hazardous waste landfill was estimated to be 1800 to 2500 RMB/tonne in China (Zhao et al., 2018), it is too costly to dispose of such huge amount of SSPR in the hazardous waste landfill.

2.3. BCR sequential extraction test of SSPR

The results of BCR sequential extraction test of raw SSPR were presented in Fig. 1. The proportion of metals in F0 followed the order of Ca (22.83%) > Mg (22.40%) > Cu (5.55%) > Cr (4.97%) > Al (1.63%), other metals in F0 were negligible. This phenomenon revealed that about one-fifth of Ca and Mg in SSPR could be dissolved in water. It was reported that Ca-containing substances in SSPR may exist as gypsum (CaSO_4) and CaF_2 (Li et al., 2014). Since CaF_2 is insoluble in water and slightly soluble in inorganic acids, it is likely that most of Ca existed in SSPR as gypsum. For Cr, former publications revealed that Cr_2O_3 , $\text{Cr}(\text{OH})_3$ and CrF_2 were the main forms in SSPR (Rögener et al., 2012; Li et al., 2014; Leonzio, 2016; Tang et al., 2018). However, all of the above three chromium compounds are insoluble in water which means they cannot be leached out by water. This is inconsistent with the leaching results in this study. Bruck et al. (2017) studied the composition of steel pickling liquor and they found that there was some of Cr(VI) in SSPR. From our former study, the total amount of Cr(VI) in SSPR was over 300 mg/kg (Su et al., 2019a). Since most of Cr(VI) can dissolve in water and thus, it is possible that the Cr exists in F0 is mainly Cr(VI).

The proportion of metals in F1 followed the order of Mg (71.53%) > Ni (61.69%) > Zn (43.67%) > Ca (31.96%) > Cr (28.32%) > Al (27.18%) > Mn (19.96%) > Cu (18.99%) > Fe (1.4%). It is obvious that much more metals become leaching available when SSPR subjected to the acid condition. The proportions of metals in F2 were Mn (73.0%) > Fe (72.16%) > Cu (62.38%) > Zn (42.42%) > Cr (37.59%) > Ni (30.11%) > Ca (24.51%) > Al (13.03%) > Mg (5.32%). It can be seen that more than half of the Fe and Mn in SSPR exist in F2. The higher proportion of Cu and

Table 2 – Concentrations of metals in raw stainless steel pickling residue (SSPR).

Metal	HJ/T 299		HJ/T 300		GB 5086.1	
	Extract (mg/L)	GB5085.3 ^a	Extract (mg/L)	GB 16889 ^b	Extract (mg/L)	GB1859 ^c
Al	ND ^d	NS ^e	117.2	NS	ND	NS
Ca	786	NS	2320	NS	904	NS
Cr	15.2	15	193.8	4.5	10.16	12
Cu	0.14	100	9.22	40	ND	75
Fe	0.124	NS	149.6	NS	ND	NS
Mg	28.5	NS	132.6	NS	23.6	NS
Mn	0.044	NS	47.4	NS	ND	NS
Ni	0.27	5	202.5	0.5	ND	15
Zn	ND	100	7.96	100	ND	75

^a Threshold for defining the waste as hazardous waste in China.; ^b Threshold for entering sanitary landfills in China.;

^c Threshold for entering hazardous waste landfills in China.; ^d Not detected.; ^e No standard threshold.

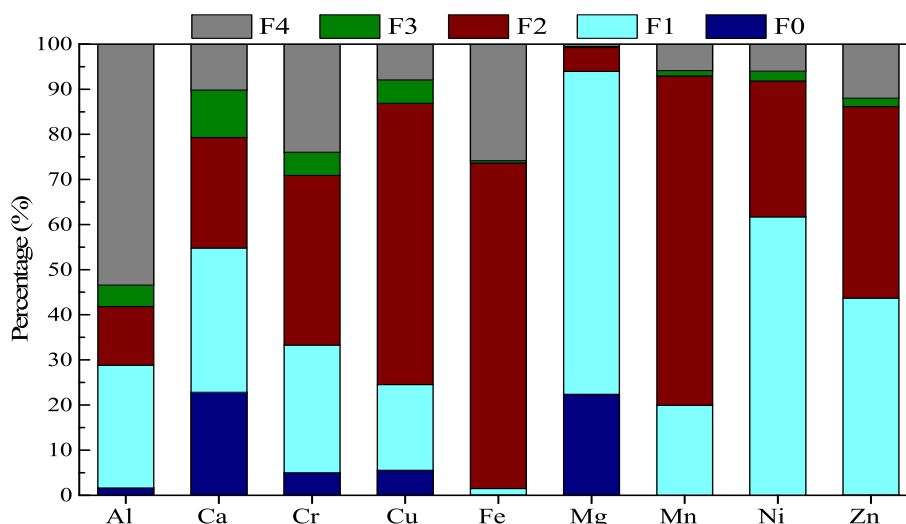


Fig. 1 – BCR sequential extraction results of stainless steel pickling residue (SSPR).

Zn in F2, and the significant increase in the proportion of Cr and Ni indicated that there was a considerable amount of these metals existed as Fe–Mn oxides. All the metals detected in F3 were very low indicated that the amounts of metal-organic compounds or metal sulfides were rare. This coincided with the nature of SSPR as a product of inorganic acids and metals. The proportion order of the metals in F4 were: Al (53.41%) > Fe (25.82%) > Cr (23.96%) > Zn (11.98%) > Ca (10.18%) > Cu (7.93%) > Ni (6.0%) > Mn (5.86%) > Mg (0.5%). As aforementioned, F4 represents the residual fraction of metals which is only soluble in very strong mixed acids (i.e., aqua regia or $\text{HNO}_3 + \text{HF} + \text{HClO}_4$). Thus, about 24% of Cr was non-leachable while only 6% of Ni cannot be leached out from SSPR.

In order to examine the precision of this modified BCR sequential leaching test, recovery rate (R, %) was determined using Eq. (1). In addition, risk assessment code (RAC, %) which is defined as Eq. (2) was used to identify the environmental risk and adverse effect of metals. Generally, $\text{RAC} < 1\%$ means the metal has “no risk” to environment, 1%–10% “low risk”, 11%–30% “medium risk” and “31%–50% “high risk”. When $\text{RAC} > 50\%$, the metal poses a “very high risk” to the environment (Wang et al., 2015; Sungur et al., 2015). The amounts of metals in each fraction, R and RAC were summarized in Table 3. The metal contents (mg/kg) in each fraction obtained by multiplying the metal concentration in

the leachates (mg/L) by the volume of the extraction fluids (40 mL for F0, F1, F2 and F3, while 10 mL for F4) and divided by the mass of the sample (1 g).

$$R = \frac{F0 + F1 + F2 + F3 + F4}{\text{Total content}} \times 100\% \quad (1)$$

$$\text{RAC} = \frac{F0 + F1}{F0 + F1 + F2 + F3 + F4} \times 100\% \quad (2)$$

From Table 3, the R values of metals varied from 93.46% to 104% except for Cu, Mn, and Zn with the R of 125.61%, 65.53% and 122%, respectively. Therefore, the amount of Cu and Zn determined by $\text{HNO}_3\text{--H}_2\text{O}_2$ -digestion were smaller than their actual values. The RAC of each metal followed the order of: Mg (93.93%) > Ni (61.70%) > Ca (54.79%) > Zn (43.71%) > Cr (33.29%) > Al (28.80%) > Cu (24.54%) > Mn (19.96%) > Fe (1.48%). Therefore, Mg, Ni, and Ca were easily soluble and thus posed “very high risk” to the environment, Zn and Cr were “high risk”, Al, Cu, and Mn were “medium risk”, and Fe was very stable and had a “low risk” to the environment.

2.4. Characterization of the chemically fixed SSPR

Fig. 2 showed the XRD patterns of raw SSPR and chemically fixed SSPR. The main compounds identified in the samples were summarized in Table 4.

Table 3 – Concentrations (mg/kg) and risk assessment code (RAC) of metals in modified European Community Bureau of Reference (BCR) sequential extraction of raw SSPR.

Metal	F0	F1	F2	F3	F4	R (%)	RAC (%)
Al	30.16	836	400.8	146.4	1643	97.03	28.80
Ca	39480	55280	42400	18200	17600	99.04	54.79
Cr	534.4	3044	4040	554	2575	93.46	33.29
Cu	37.32	127.6	419.2	34.6	53.3	125.61	24.54
Fe	71.44	1204	62120	459.2	22230	97.6	1.48
Mg	839.13	2680	199.34	9.65	18.52	104.0	93.93
Mn	0.2	1108	4052	65.6	325	65.53	19.96
Ni	0.32	5520	2548	184.8	508	96.15	61.70
Zn	0.16	173.12	168.16	7.48	47.5	122.0	43.71

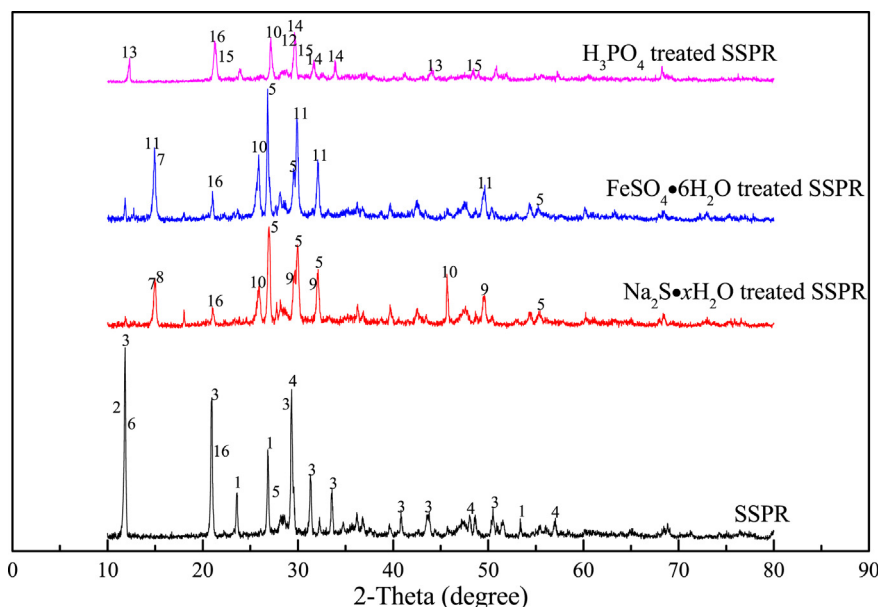
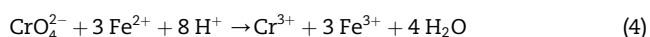
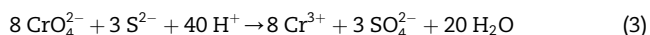
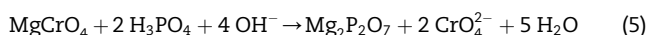


Fig. 2 – XRD patterns of raw SSPR, $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ -fixed SSPR, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -fixed SSPR and H_3PO_4 -fixed SSPR (1: MgCrO_4 , 2: $\text{Fe}_2\text{Ni}_2\text{CO}_3(\text{OH})_8 \cdot 2\text{H}_2\text{O}$, 3: Gypsum, 4: CaF_2 , 5: CrF_2 , 6: $\text{Fe}_6(\text{OH})_{12}\text{CO}_3$, 7: FeF_3 , 8: $\text{Na}_2\text{Al}_{0.5}\text{Fe}_{9.5}\text{O}_{15}$, 9: $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, 10: $\text{Ni}(\text{HCO}_3)_2$, 11: CaSO_4 , 12: $\text{Mg}_2\text{P}_2\text{O}_7$, 13: $(\text{Mn,Ca})_3\text{Mn}_{12}\text{O}_{27} \cdot 15\text{H}_2\text{O}$, 14: CaCO_3 -Calcite-III, 15: $\text{Mg}_{0.1}\text{Ca}_{0.9}\text{CO}_3$, 16: $\text{Ni}(\text{NO}_3)_2$).

Obviously, the raw SSPR was dominated by gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and CaF_2 . Cr mainly existed as CrF_2 , while MgCrO_4 ($2\theta = 23.6^\circ, 26.7^\circ, 28.2^\circ, 29.5^\circ, 40.7^\circ$ and 54.2° , PDF 21–1256) was also identified in raw SSPR. Since CrF_2 is insoluble in water and MgCrO_4 has a solubility of 137 g/100 mL in water at 20°C (Wikipedia contributors, 2018), it is likely that the leaching concentration of Cr in water extraction test was Cr(VI). This is in line with former studies (Li et al., 2014; Su et al., 2019a). Fe was found to be $\text{Fe}_2\text{Ni}_2\text{CO}_3(\text{OH})_8 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_6(\text{OH})_{12}\text{CO}_3$ in the SSPR. For Ni, its main form in SSPR was $\text{Fe}_2\text{Ni}_2\text{CO}_3(\text{OH})_8 \cdot 2\text{H}_2\text{O}$. After fixation using $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was converted to calcium sulfate hydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). This could be caused by the change of the number of water molecules combined with CaSO_4 during the fixation. The most important change was that MgCrO_4 was not found in the chemically fixed products. For $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ - and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -fixed product, it is reasonable to draw the conclusion that both $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ can reduce Cr(VI) to Cr(III) as shown in Eqs. (3) and (4), and $\text{Cr}(\text{OH})_3$ was formed eventually.



However, according to Rai et al. (1987), $\text{Cr}(\text{OH})_3$ was amorphous and remained amorphous throughout the equilibration period. This could be the main reason that $\text{Cr}(\text{OH})_3$ was not identified in both SSPR and fixed SSPR in this study. For phosphoric acid-fixed SSPR, MgCrO_4 was not identified either. However, $\text{Mg}_2\text{P}_2\text{O}_7$ was detected in the phosphoric acid-fixed SSPR. Since Mg existed as MgCrO_4 in raw SSPR, the main reaction could be:



The microscope morphology of raw SSPR and treated SSPR were presented in Fig. 3. As it can be seen in Fig. 3a, raw SSPR was dominated by a large volume of flocks with scattered particles and there was no crystal structure in it. With treatment of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, the product was filled with highly clump crystals (Fig. 3b). In contrast, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -fixed SSPR contained plate and column structure, and the size varied from 5 nm to 15 μm (Fig. 3c). There was prism-like structure appeared in the phosphoric acid-fixed SSPR.

2.5. Leaching toxicity of the chemically fixed SSPR

2.5.1. Toxicity extraction test of fixed SSPR

As aforementioned, Cr was the only metal that exceeded the regulated limits of for hazardous waste identification and the

Table 4 – The main compounds identified in the samples using XRD analysis.

Sample	Compound
Raw SSPR	CaF_2 , CrF_2 , MgCrO_4 , $\text{Ni}(\text{NO}_3)_2$, $\text{Fe}_2\text{Ni}_2\text{CO}_3(\text{OH})_8 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ -Gypsum, $\text{Fe}_6(\text{OH})_{12}\text{CO}_3$ - Green Rust
$\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ -fixed SSPR	FeF_3 , CrF_2 , $\text{Ni}(\text{HCO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Na}_2\text{Al}_{0.5}\text{Fe}_{9.5}\text{O}_{15}$, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ -Calcium Sulfate Hydrate
$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -fixed SSPR	FeF_3 , CrF_2 , $\text{Ni}(\text{HCO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, CaSO_4 - Calcium sulfate (VI)
Phosphoric acid-fixed SSPR	$\text{Mg}_2\text{P}_2\text{O}_7$, $\text{Ni}(\text{HCO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Mg}_{0.1}\text{Ca}_{0.9}\text{CO}_3$, CaCO_3 - Calcite-III, $(\text{Mn,Ca})_3\text{Mn}_{12}\text{O}_{27} \cdot 15\text{H}_2\text{O}$

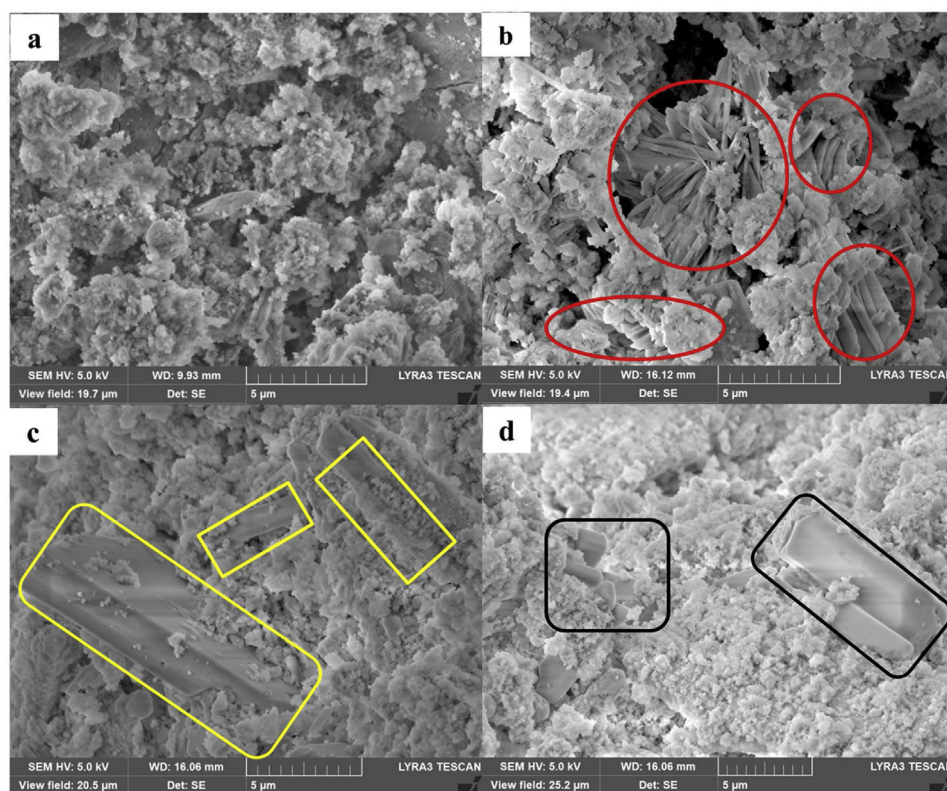


Fig. 3 – Micro-structure of (a) SSPR, (b) $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ -fixed SSPR, (c) $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -fixed SSPR and (d) H_3PO_4 -fixed SSPR. The red marked area in Fig. 3b shows highly clump crystals after treatment by $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, the yellow marked area in Fig. 3c shows the plate structure after treatment by $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, and the black marked area in Fig. 3d indicates the prism-like structure appeared in H_3PO_4 -fixed SSPR.

standard for entering sanitary landfill. In the meanwhile, Ni exceeded the regulated limit of the standard for entering sanitary landfill. Therefore, the fixation focused on Cr and Ni in this study. The leaching amount of Cr and Ni are shown in Fig. 4. The related thresholds for hazardous identification, entering sanitary landfills and entering hazardous waste landfill were also shown as the red line in the figures. The thresholds for beneficial use of SSPR in roadbed materials, concrete and cement aggregates for Cr and Ni were defined based on China HJ/T 301- Environmental Protection Technical Specifications for Pollution Treatment of the Chromium Residue. The specific value for Cr and Ni were 1.5 and 0.5 mg/L in the sulphuric acid and nitric acid extraction (Su et al., 2019a).

As shown in Fig. 4a, after fixation by $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, the concentrations of Cr in the sulphuric acid and nitric acid extraction were lowered to below the beneficial use threshold of 1.5 mg/L. However, the results from phosphoric acid-treated SSPR were significantly different. When the phosphoric acid dose ranged from 4% to 6%, the leaching concentrations of Cr were 41.5 and 29.8 mg/L, respectively, which were even higher than that for the raw SSPR (15.2 mg/L). The similar phenomenon was also found by Quina et al. (2010). They studied the stabilization of different metals in municipal solid waste by phosphoric acid and found that when the liquid to solid ratio ranged from 20 to 200 L/kg, the leaching concentration of the sample increased overall. In addition, according to Eq. (5), MgCrO_4 can react with

phosphoric acid to produce CrO_4^{2-} which is highly soluble. This might be the reason that after phosphoric acid fixation, the leaching concentrations of Cr increased significantly. When the dosage of phosphoric acid increased to 8% and 10%, the leaching concentrations of Cr were 8.62 mg/L and 7.72 mg/L, respectively, which were still higher than the beneficial use threshold.

The leaching concentrations of Ni in sulphuric acid and nitric acid extraction tests were shown in Fig. 4b. Point of 4% $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ - and 3% $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -treated SSPR were not given in the figure because the concentrations were below the detection limit. It is obviously that the leaching concentration of Ni in $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ - and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -treated SSPR passed the threshold of beneficial uses of 0.5 mg/L. In addition, the fixation performance of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ was better than that of $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$. Taking account of Cr and Ni together, the SSPR fixed by $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ can be safely used as roadbed materials, concrete and cement aggregates with respect to the leaching concentrations. For phosphoric acid-treated SSPR, when the phosphoric acid concentration was 4% and 6%, the concentrations of Ni were below the threshold. It is stressed out that the concentrations of Ni after treatment with 8% and 10% phosphoric acid were higher than that of raw SSPR, indicating that excessive amount of phosphoric acid may promote the leaching of Ni.

As shown in Fig. 4c and Fig. 4d, there were significant decreases in the concentrations of Cr and Ni in acetic acid buffer

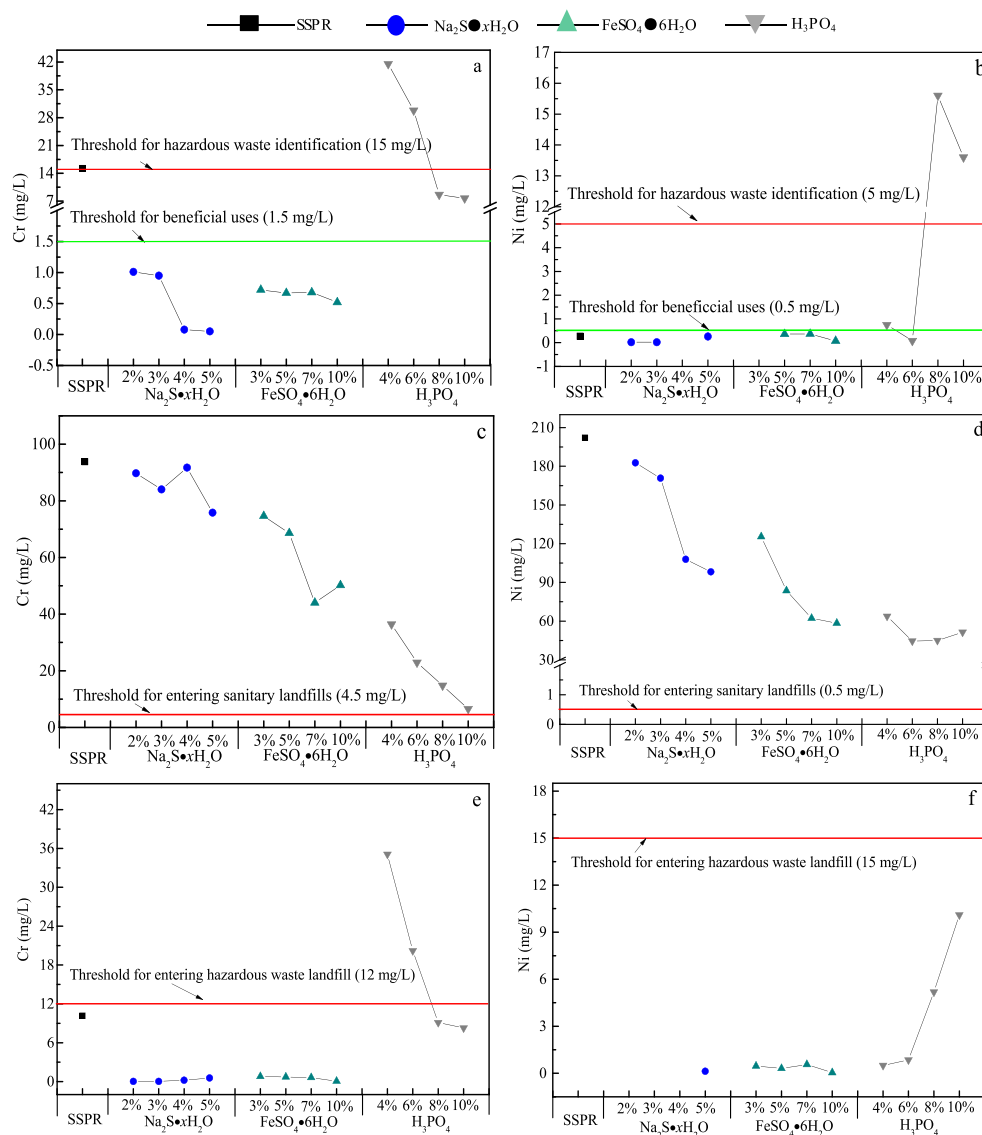


Fig. 4 – Leaching concentrations of Cr (a, c, e) and Ni (b, d, f) in HJ/T 299, HJ/T 300, and GB 5086.1 after fixation by $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$, and H_3PO_4 .

solution extraction after fixation using phosphoric acid. When the concentration of phosphoric acid was 10%, the leaching concentration of Cr was 6.54 mg/L, indicated that about 93% of Cr was immobilized as compared to that of raw SSPR. In concern of Ni, when the amount of phosphoric acid was 6%, the leaching concentration of Ni was 44.5 mg/L. It should be stressed herein that the phosphoric fixation can reduce the leaching concentration of Cr and Ni dramatically than the fixation of $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$.

The leaching concentrations of Cr and Ni in water extraction were shown in Fig. 4e and Fig. 4f, respectively. It can be seen in Fig. 4e that the leaching concentrations of Cr after fixation by $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ were less than 1 mg/L, indicating $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ were very effective in reducing the mobility of Cr. In contrast, the performance of phosphoric acid was very poor. When the phosphoric acid concentration was 4% and 6%, leaching concentrations of Cr were 35.1 and 20.2 mg/L, respectively.

These values were much higher than the threshold of 12 mg/L as well as the original concentration of 10.16 mg/L in SSPR. The similar leaching performances of sulphuric acid and nitric acid extraction and acetic acid buffer solution extraction after fixation by phosphoric acid indicated that phosphoric acid could make the leaching of Cr more easily in water extraction. With the concentration of phosphoric acid increased to 8% and 10%, the leaching concentration of Cr was lower than the threshold of 12 mg/L. For Ni, as shown in Fig. 4f, there was no potential risk posed by raw SSPR. Even though more Ni was leached out from the fixed samples, their concentrations were below the regulated threshold.

2.5.2. BCR sequential extraction test of fixed SSPR

The speciation of Cr and Ni in SSPR after fixation was shown in Fig. 5. As seen in Fig. 5a, Cr was mainly found in F4 with percentage of 47.81%, 49.35%, 59.93% and 61.09% after treatment

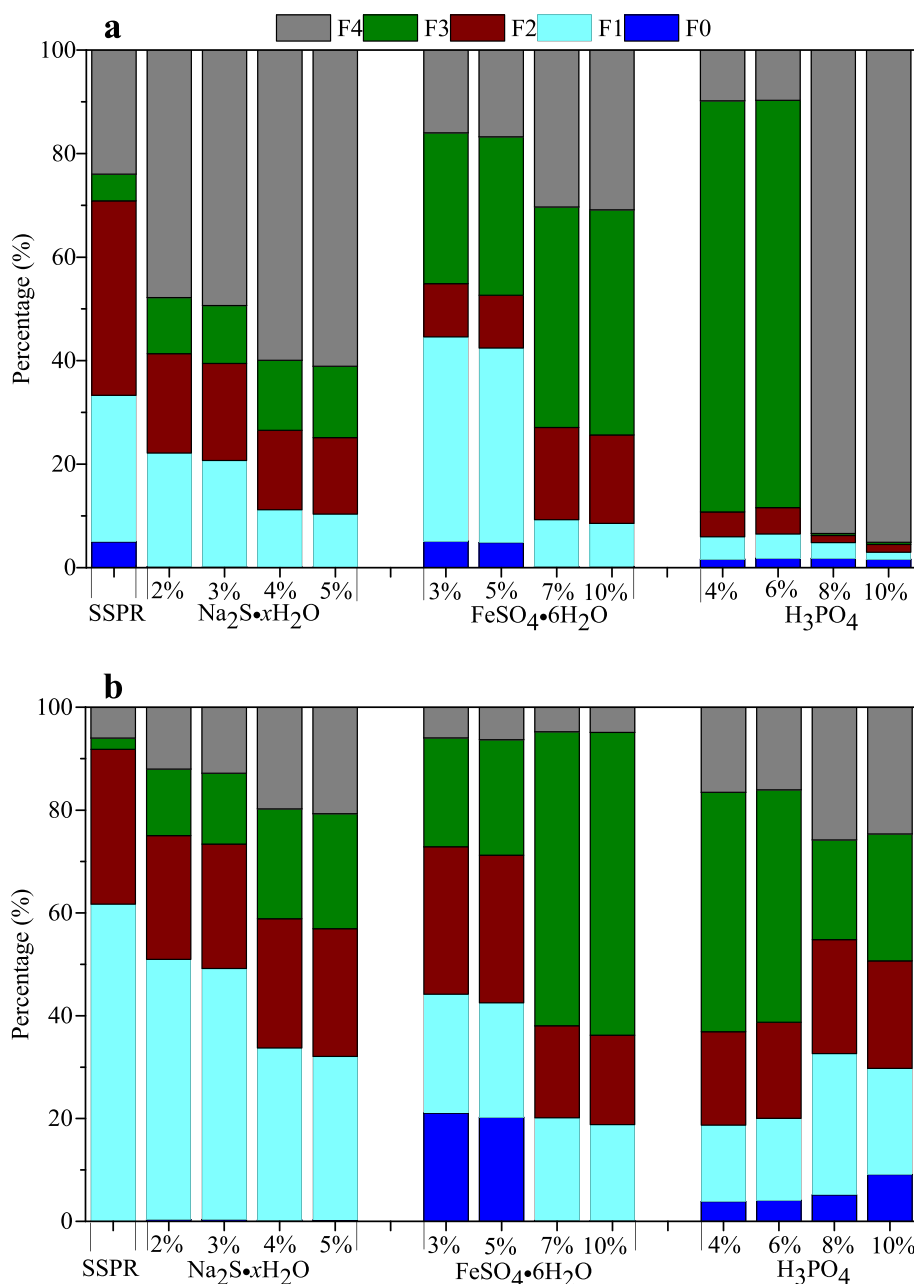


Fig. 5 – BCR sequential extraction results for Cr (a) and Ni (b) in $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ -, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -, and H_3PO_4 -fixed SSPR.

with 2%, 3%, 4% and 5% $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, respectively. As expected, the share of Cr in F0 significantly decreased after fixation (less than 0.5%), thus the amount of water-soluble Cr was reduced. With the increase of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ addition, the proportion of F1 decreased gradually from 21.93% to 10.25%. The speciation of Cr in $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ treated SSPR showed that when the amount of $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ were 3% and 5%, Cr accounted for the largest proportion in F1 in the treated SSPR (39.47% and 37.58%, respectively), followed by F3 (29.16% for 3% and 30.62% for 5%). When the addition of $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ was 7% and 10%, Cr was mainly presented in F3 with a percentage of 42.63% and 43.48%, respectively. In phosphoric acid fixation, about 80% of Cr was in F3 when the phosphoric acid concentration was 4% and 6%. When the concentration of phosphoric acid was 8% and 10%,

more than 90% of Cr were distributed in F4 (93.41% and 95.09%, respectively). Normally, the greater the proportion of Cr in the residual fraction, the smaller the leaching concentration would be. However, the concentration of Cr in the sulphuric acid and nitric acid extraction and water extraction of phosphoric acid-fixed SSPR was much higher than that of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ - and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ -fixed SSPR.

For Ni, as shown in Fig. 5b, F2 held the majority after $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ treatment, 50.58%, 48.86%, 33.50% and 31.86% for 2%, 3%, 4% and 5% of $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ -fixed SSPR, respectively. Besides, F3 and F4 varied from 12.93% to 22.35% and 12.04%–20.72%. The most significant change of Ni in SSPR after fixation by $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ was the increase in the proportion of F3. Up to 60% of Ni existed in F3 after fixation using 8% and 10% of

Table 5 – RAC of Cr and Ni in SSPR after fixation by $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ and phosphoric acid.

Sample	RAC (%)	
	Cr	Ni
2% $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$	22.14	50.95
3% $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$	20.73	49.21
4% $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$	11.12	33.74
5% $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$	10.34	32.1
3% $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$	44.57	44.19
5% $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$	42.44	42.53
7% $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$	9.27	20.15
10% $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$	8.56	18.82
4% Phosphoric acid	5.96	18.74
6% Phosphoric acid	6.51	20.05
8% Phosphoric acid	4.82	32.64
10% Phosphoric acid	2.99	29.76

$\text{FeSO}_4\cdot 6\text{H}_2\text{O}$. The same phenomenon was also found in phosphoric acid-fixed SSPR. It is worth noting that the distribution of Ni in F1 increased gradually (from 3.5% to 9.1%) in the sample after phosphoric acid treatment. In this way, phosphoric acid-fixed SSPR was more likely to release Cr in acid condition.

The RAC of Cr and Ni after fixation are given in Table 5. In general, the RAC of Cr and Ni decreased gradually with the increase of the $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ amount. When the $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ amount was 5%, the RAC of Cr and Ni were 10.34% and 32.1%, respectively. As a result, Cr posed “low risk” and Ni posed “high risk” to the environment. In the sample of 10% $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ -fixed SSPR, the RAC of Cr and Ni were 8.56% and 18.82%, respectively, and therefore Cr had “low risk” and Ni had “medium risk” to the environment. The RAC of Cr in 10% phosphoric acid treated SSPR were less than 11% indicated that it was “low risk” to the environment. For Ni, its RAC in phosphoric acid treated SSPR ranged from 18.74% to 32.64% meant it posed “medium” to “high” risks to the environment.

3. Conclusions

In this study, the leaching concentration of different metals in SSPR was determined by three different single extraction and BCR sequential extraction. The risk assessment code of the metals was also determined. We also studied the chemical fixation performance of $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$, and H_3PO_4 on the toxic metals. The results indicated that SSPR is a hazardous waste with respect to its leaching toxicity. Cr was identified as the most toxic heavy metal due to its total amount was 11,500 mg/kg and the leachable Cr was MgCrO_4 in SSPR. BCR sequential extraction showed that Cr in SSPR mainly existed as F1 (28.32%), F2 (37.59%) and F4 (23.96%), and its RAC was 33.29% indicated Cr posed “high risk” to the environment. The total amount of Ni was found to be 8800 mg/kg and primarily existed in acid-soluble form (61.69%), the RAC of Ni was 61.7%, indicating it posed “very high risk” to the environment.

After fixation by $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$, the leaching concentration of all the metals in both sulphuric acid and

nitric acid extraction and water extraction were much lower than the related limits. Especially for Cr, after fixation by $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$, its leaching concentration was less than 1.5 mg/L. The main mechanism for $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ fixation was found to be the strong reducing ability of S^{2-} and Fe^{2+} that can reduce Cr(VI) to Cr(III). Consequently, the $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ - and $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ -fixed SSPR could be safely reused as roadbed materials, concrete and cement aggregates.

4. Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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