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Study on Removal and Solidified Characteristics of Heavy Metals in the Slag from High Temperature Smelting of Copper Sludge, Electroplating and Pickling Sludge

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Abstract. The slag from high temperature smelting of copper sludge, electroplating and pickling sludge in different cooling methods were studied for the heavy metal removal and solidification effect. The contents results showed large removal of Cu, Ni, Cd and serious enrichment of Mn, Ba, Be, Pb, As. The leaching results showed the best solidification effect of Cu, Ni, Cd and the poorest of Ba. XRD showed more crystal structures in RW and JF, while little in SH and MF, which had no different effect on solidification. SEM-EDS results showed dense surface in copper sludge disposal enterprises' slag samples, and various-materials surface in electroplating and pickling sludge disposal enterprises' slag samples. The solidification effect of slag produced from smelting sludge was poor in acid environment while better in weak acid to alkaline environment.

Introduction

Copper sludge, electroplating and pickling sludge are two kinds of solid waste produced by treating copper wastewater, electroplating wastewater and pickling wastewater, which are considered to be hazardous waste due to their toxic heavy metals such as Cu, Zn, Cr, Pb, Cd and so on. Common disposal methods are wet, dry, wet and dry treatment, such as solidification/ stabilization, heat treatment and so on. [1]

The high-temperature melting technique in dry treatment is usually carried out by adding additives such as charcoal, limestone, dolomite, iron ore at a temperature of 1300 °C or above [2,3] to smelt the sludge by means of high temperature and reducing agent with the oxide being reduced to elemental metal and the rest becoming slag. Generally, metal will sink into the bottom of the melting furnace after smelting because of its relatively high density to slag and will form metal ingots after cooling. While the slag in the upper part of the smelting furnace has a relatively low density, which contains a small amount of non-reduced metal oxide and a few low-density metals, and is discharged from the furnace in a molten state and cooled down to form dry slag. The sludge volume can be reduced by high temperature smelting treatment of copper sludge, electroplating and pickling sludge disposal with the extraction of metal in the sludge to achieve resource utilization. [4]

Natural cooling and water quenching are two cooling methods for high temperature melting slag. The initial crystallization of the slag melts can be grown in the form of dissolution-precipitation with the slow natural cooling rate to form a good euhedral or subhedral crystal. [5] Water quenching using a certain pressure of the flow through the rapid cooling of the slag in a short period of time breaks the molten slag, to form the slag block of amorphous structure, which is usually glass-based. [6] The vitrified residue is a black light translucent glassy solid. [7] In general, the slag formed a glassy structure in the smelting process for joining slag flux under high temperature. The formation of glassy structure, and the residual heavy metals and metal oxides are encapsulated in a dense grid of glassy

residue with the limited migration into the environment, [7, 8] thus to stabilize the heavy metal in the slag, and achieve the solidification to avoid environmental pollution.

Many people have made a series of experiments on the slag produced after high temperature smelting. [9] However, there are few studies on the solidified effect of heavy metals on slag produced by different sludge sources and obtained by different cooling methods.

The slags produced by four enterprises in Jiangsu province of cooper sludge, electroplating and pickling sludge disposal by high temperature melting were collected and studied. The heavy metal content and leaching toxicity of sludge and the slag were analyzed to investigate the enrichment rate and solidified character of heavy metals in the slag. The slags were analyzed by XRD crystal phase analysis and SEM-EDS surface morphology and energy spectrum analysis, and the microstructure of slag produced by high temperature melting was explored. Moreover, the leaching characteristics of heavy metals in slag were studied in different pH leaching solutions, to investigate the solidification characteristics of heavy metals in slags for different kinds of sludge and different cooling methods.

Materials and methods

Samples. The residue samples marked as RW, JF, SH, MF were collected seven times from four enterprises for the disposal of copper sludge, electroplating and pickling sludge by high temperature smelting. RW, JF were enterprises of disposal of copper sludge with the natural cooling method of slag, while SH、 MF were enterprises of disposal of electroplating and pickling sludge with the water quenching method of slag. These four enterprises' disposal technological process were basically the same except for individual working conditions.

Heavy metal content analysis. The contents of Cu, Cr, Ni, Zn, Mn, Ba, Co, Pb, Cd, Be, As and Se in the samples were determined by microwave digestion. 0.100-0.200g dry sample was put in 50mL Teflon digestion tube, adding 5mL nitric acid, 2mL perchloric acid, 2mL hydrofluoric acid, covered the acid to the white smoke exhaustion by adding 0.5 mL boric acid, then placed in graphite digestion instrument 160 ℃ overnight and transferred to a volume of 50 mL, and then tested the content of heavy metals three times by the inductively coupled plasma mass spectrometry (ICP-MS).

Leaching toxicity test. According to the method in the standard 'Solid waste-Extraction procedure for leaching toxicity-Sulphuric acid & nitric acid method' [10], 100g of dry sample was weighed, and the mixed acid (pH = 3.2) was added at the ratio of solid to liquid 1:10. The flocculation was carried out for 18h. Leaching toxicity test was performed three times by ICP-MS. Same experiments were carried out in other mixed acid (pH = 1.0). The results of the leaching toxicity test were compared in the standard 'Identification standard for hazardous wastes-Identification for extraction toxicity' [11].

Characterization of slag. The crystalline phases of slag samples were analyzed using X-ray diffraction (XRD) with diffractometer at 40 kV and 100 mA between 5 and 80° (2θ) at a step size of 0.02°. The surface morphology of the slag samples was observed using a scanning electron microscope (SEM) operated at 2.0 KV connected with electron dispersive spectrometer (EDS) to qualitatively describe the elements in the slag.

Data analysis. The contents and leaching toxicity of metal in the sludge and slag samples were analyzed by SPSS 22.

Results and discussion

Heavy metal content in the sludge and slag. The comparison of major heavy metal contents in the sludge and slag samples is shown in Fig 1. It is found that the copper sludge treated by RW and JF mainly contained Cu with a small amount of Zn, Mn, and the slag obtained by high temperature melting mainly contained Cu, Ba, and Mn. While the electroplating and pickling sludge treated by SH and MF mainly contained Cr, Zn, Ni, Mn, and the slag obtained by high temperature melting mainly contained Cr, Zn, Ba, Ni and Mn.
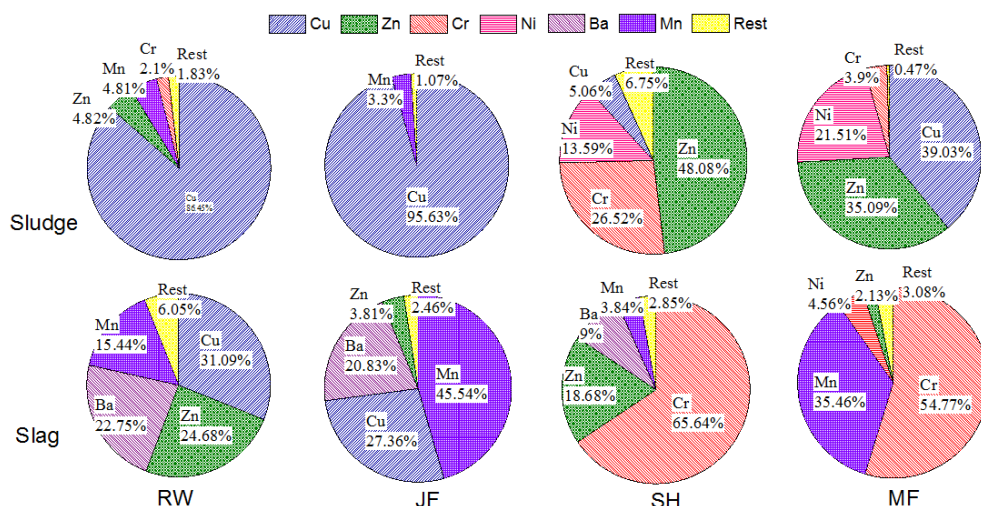
Fig. 1 Comparison of main heavy metal contents in sludge and slag of four enterprises

It can be seen clearly from Fig. 1 that the slag produced by the high temperature smelting of the copper sludge disposal from RW and JF contained Cu and a large amount of Mn, Ba, Zn. And the slag from SH and MF by the high temperature smelting produced more Cr, and the relative content of Mn was also increased. Thus, the content of heavy metals in the slag was compared to the content in the dry sludge to obtain the enrichment rate *P* of heavy metals in slag after high temperature smelting of sludge, seen in Eq. 1. It indicates that the sludge has been enriched by the smelting of heavy metal when the value is greater than 1, while it indicates that the metal in the sludge is separated from the slag after high temperature melting when the value is less than 1, and the results of enrichment rate of heavy metals in four enterprises are shown in Table 1.

$$P = \frac{M_{slag}}{M_{sludge}}. \tag{1}$$

Where M_{slag} refers to the metal content in the slag (mg/kg); M_{sludge} refers to the metal content in the sludge (mg/kg).

Table 1. Enrichment rate of heavy metals

	RW	JF	SH	MF
Cu	0.065362	0.045058	0.074698	0.002064
Cr	0.426866	1.430564	1.383333	1.341085
Ni	0.257821	0.132518	0.064656	0.020253
Zn	0.931079	2.299303	0.217241	0.005804
Mn	0.583347	2.175379	1.284768	15.99252
Ba	3.687151	14.80153	4.417476	4.996035
Co	0.428529	1.755107	0.174938	0.0714
Pb	3.208019	0.346522	0.008486	0.261331
Cd	0.03064	0.105803	0.100314	0.289837
Be	6.804931	2.113527	1.065024	2.162967
As	2.414305	4.611685	0.390873	0.814925
Se	*1.713854*	*1.069024*	0.772318	9.767511

Table 1 indicates that the oxides containing Cu, Ni and Cd were reduced to metal by high temperature melting, precipitating to the bottom of the furnace and separated from the slag. Cr, Zn, Pb, Mn, Co and As produced enrichment in some samples, but the enrichment rate of Cr, Zn, Co and Pb was smaller, while Ba appeared obvious enrichment effect. In addition, Mn of MF appeared a serious enrichment after the high temperature smelting. Combined with Figure 1, it is found that the slag appeared in more Ba, while MF's slag still appeared in more Mn after the high temperature melting. Therefore, the analysis was combined with statistical methods.

Pearson correlation analysis of heavy metal content in sludge and slag was carried out with the results shown in Table 2

Table 2. Correlation between heavy metals contents in slag and sludge

	Cu	Cr	Ni	Zn	Mn	Ba	Co	Pb	Cd	Be	As	Se
Pearson Correlation	0.665	0.996**	0.935	-0.323	0.018	0.701	0.954*	-0.363	0.304	-0.367	0.993**	0.096
Sig. (2-tailed)	0.225	0.004	0.065	0.677	0.982	0.299	0.046	0.637	0.696	0.633	0.007	0.904

It can be seen from Table 2 that only the contents of Cr and As in the slag and sludge were positively correlated at the significance level of 0.01, with the strong correlation coefficients of 0.996 and 0.993 respectively and the content of Co in the slag and sludge was correlated at the significance level of 0.05, with the same strong correlation coefficients of 0.996, indicating that the contents of Cr, As, Co in the slag after high temperature smelting were affected by their contents in the sludge, while others were affected by the process.

The results show that Cu, Ni and Cd were removed by high temperature smelting with Zn and Co being basically removed except for individual samples, and As was removed from the two enterprises that deal with electroplating and pickling sludge, while Mn, Ba, Be Cr and Se showed a serious enrichment phenomenon.

Leaching toxicity at formal standard environment. The leaching toxicity were executed in standard acid environment (leaching solution pH = 3.2), and all of the leaching toxicity of slags and sludge was within the standard range. For the clearer analysis, the ratio of heavy metal leaching toxicity in slag to sludge was calculated to obtain slag and sludge leaching toxicity ratio R, see in Eq. 2.

$$R = \frac{T_{slag}}{T_{sludge}}.$$
(2)

Where T_{slag} refers to a metal leaching toxicity of slag (mg/L); T_{sludge} refers to a metal leaching toxicity of sludge (mg/L).

The ratio of heavy metal's leaching toxicity of slag and sludge is shown in Table 3. The data of Pb and Be was not shown because they were not detected in the sludge and slag of all enterprises' samples.

Table 3. The ratio R of heavy metal leaching toxicity of slag and sludge

	RW	JF	SH	MF
Cu	0.0005	0.0049	0	0.1139
Cr	0.0950	2.9120	0.0101	0.2352
Ni	0	0.0117	0.7676	0.0278
Zn	0	0	*0.282*	0
Cd	0	/	0	/
As	2.1995	0.4150	0.1433	4.8556
Se	/	/	0	/
Ba	*2.19*	*0.34*	3.3083	*0.05*
Fluoride	4.6492	1.2638	6.4457	1.5149
Cr^{6+}	/	/	/	0

From the table 3, we can see that, compared with the leaching toxicity of heavy metals in slag and sludge, the leaching ratios of Cu, Ni and Cd were all less than 1, which indicated that high temperature melting had good effect on the solidification of these three metals. In addition to a larger proportion of the phenomenon of Cr and Zn in one enterprise, the rest showed a good solidification effect. As's leaching in JF and SH was relatively small, which may be related to the difference of

production conditions in different enterprises, and there was less detection of Se, Cr^{6+} themselves in sludge leaching with none detection of leaching in slag after high temperature melting. While the ratio of slag to sludge of Ba and fluoride is relatively large indicating that these two elements had a poor solidification effect after the high temperature melting, which may be related to the high content of Ba in slag. Thus, the pearson correlation analysis of the leaching toxicity and contents of heavy metal in slag was carried out with the results shown in Table 4.

Table 4. Correlation between leaching toxicity and contents of heavy metal in slag

	Cu	Cr	Ni	Zn	Cd	As	Ba
Pearson Correlation	-0.484	0.221	0.185	0.202	0.114	0.619*	0.663*
Sig. (2-tailed)	0.132	0.513	0.586	0.551	0.739	0.042	0.026

It can be seen from Table 4 that only the leaching toxicity and contents of Cr and As in the slag were positively correlated at the significance level of 0.05, with the strong correlation coefficients of 0.619 and 0.663 respectively, which can be seen that the high content of Ba in slag contributed to the relatively higher leaching toxicity in slag than sludge compared with the Table 3.

XRD spectroscopy. The XRD characteristics of the four samples are shown in Fig. 2. It can be seen from Fig. 2 that the XRD patterns of the natural cooling slag RW and JF showed more diffraction peaks, indicating that more crystal structures were formed. While the water quenched slag SH and MF appears less peak, indicating the less crystal, and MF slag was not detected the crystal structure, basically the glass diffraction peak. The molten slag formed under the strong impact of cold water is basically a glassy structure, while the naturally cooled slag is cooled slowly to produce more crystals. Qin et al. mentioned in the study of molten yellow phosphorus slag that water quenching slag was glass-based, and from the lithofacies analysis, we could see that the vitreous content was 85% to 90% with quartz, pseudo wollastonite, calcite, and fluorine calcium in the crystalline phase. [12]

The main crystal structure of slag from RW were KC and $K_6Fe_2O_5$, and JF's slag mainly contained $K_6Fe_2O_5$, while SH's slag mainly contained $MgFeAlO_4$.
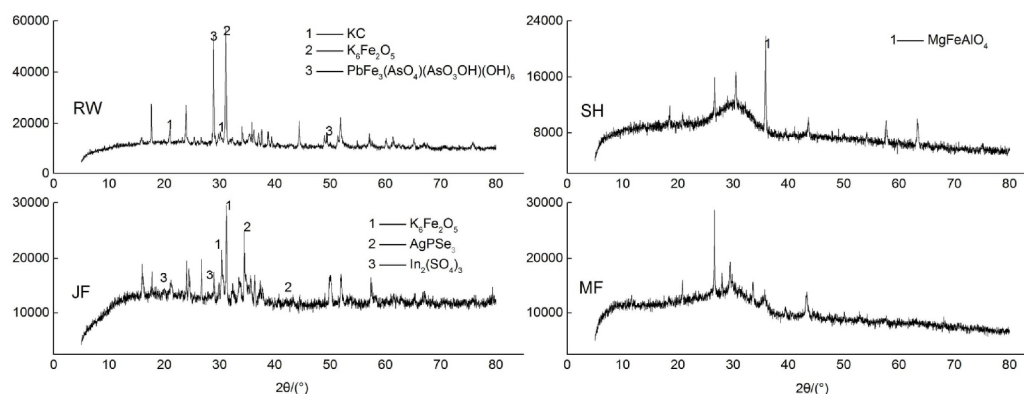

Fig. 2 XRD patterns of four samples

Huang et al. mentioned in the study on mineralogy of water quenching slag in the copper reflector that Cu not detected in XRD was probably mixed in the glass state and cannot be detected for the little content in the slag and small particle size. [13] Most of the dangerous elements studied in this paper do not form detectable crystal structures for the small amount in the slag, which means most of them may enter a glassy structure. By the solidification of the structure, leaching toxicity of slag in the standard test was far below the standard, showing a good solidification effect. However, the quenching cooling slag has no advantage over natural cooling slag on the solidification effect of heavy metals, with the only difference in structure.

SEM-EDS. As shown in Fig.3, the appearance of the selected slag from four samples was analyzed. The surface of RW and JF is dense, with different forms of material in a few places. The results of EDS analysis show that the main elements of (b) are Si, Ca and Fe, and Fe, Si, Ca and Al are the main elements of (e) with the same results of (d) basically. The surface of SH and MF showed

various forms of materials. And for SH, some of the surface showed a similar spherical material [sees in (g)], with its element content was mainly Ca, Si, Al, F, Zn, and some surface showed flocculent [sees in(h)], with the main element Ca, Si, Al, and Fe. For MF, some of the surface showed cotton swab [sees in (j)], with its element content mainly Fe, Si, Ca, Mg, Ni, and some surface showed ball-like flocculent [sees in(h)], with the main element Si, Fe, Mg and Al. The presence of such conditions may be related to the different types of sludge they were disposed of. Copper is the main element in the copper sludge with a relatively simple composition for electroplating and pickling sludge, thus when most of the Cu is extracted after the high temperature smelting there were only a small part of the Cu and a small amount of other heavy metals in the slag. The substance of the same kind of elements may exhibit different morphologies, such as (d) and (e), indicating that the same element formed into different structures of the material after high temperature smelting.
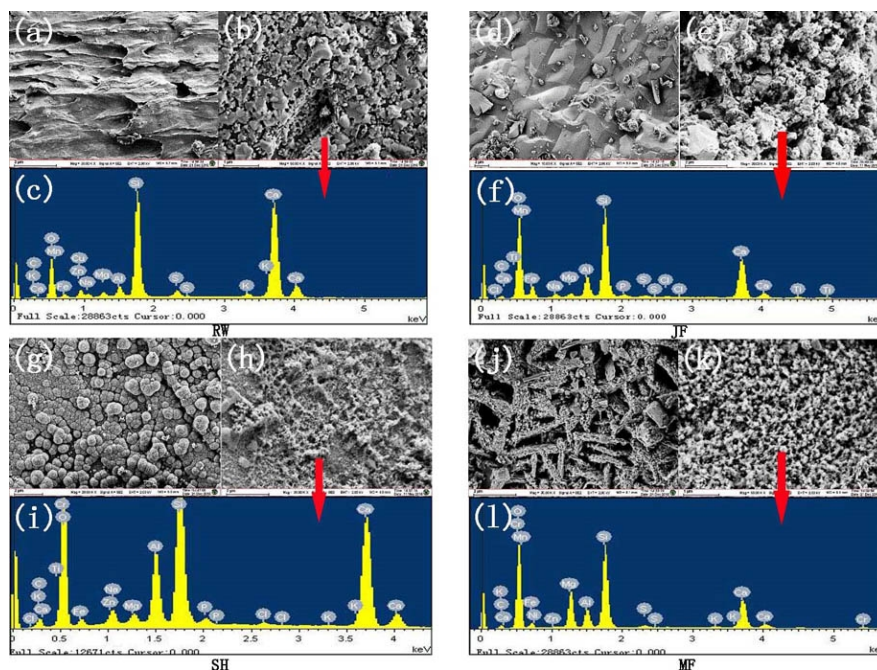

Fig. 3 SEM-EDS analysis of four samples

Leaching toxicity in different pH leaching solution. In order to investigate the solidification effect of metals in different acid and alkaline environments, different pH solutions were set to test the leaching toxicity of heavy metals in the slag with the results shown in Fig 4. As, Ba and Se are not shown for their much lower data from the standard limits in all different pH solutions. It can be seen from Fig. 4 that the Cd, Pb, Cu, Cr, Ni and Zn were almost all leaching under acidic conditions, while less leaching under neutral and alkaline conditions. There was a sharp decrease from pH 1 to pH 2, a slowly decreased from pH 2 to pH 3.2, and the stabilization of leaching toxicity from pH 3.2. Cd, Pb and Cu were largely leached under acidic conditions, while none sample appeared to exceed the standard. For Cd, RW and JF had the maximum leaching at pH 1, whose element contents in the slag were smaller than those in SH and MF, indicating that the solidification effect of RW and JF on Cd was poorer than SH and MF. Pb in MF showed a large leaching in the case of not exceeding the standard with its own high content in the slag. Pb was not detected leaching toxicity data in all samples under the standard method (pH = 3.2), which indicated that the solidification effect of slag on Pb was better under weak acid condition, while weakened under strong acid condition with a large overflow of Pb. Cu of RW and JF also appeared a lot of leaching when the pH was 1, while SH and MF's were basically 0, which was probably due to RW and JF's disposal of copper sludge, with the high Cu content itself. When the slag was disabled to solidify metal in strong acid conditions, there would be a large number of Cu overflow. For Cr, Ni and Zn, a large amount of leaching of some samples occurred when pH was 1. Therefore, the Fig.4 removed some sites (Cr and Ni in MF, Zn in RW, JF and SH) at pH 1, showing the leaching characteristics of slag under different pH leaching solutions. Cr (1), Ni (1) and Zn (1) in Fig. 4 show that the leaching toxicity of heavy metals still

tended to decrease from the acid solution to the alkaline solution, and only Cr had a slight fluctuation near pH 7.
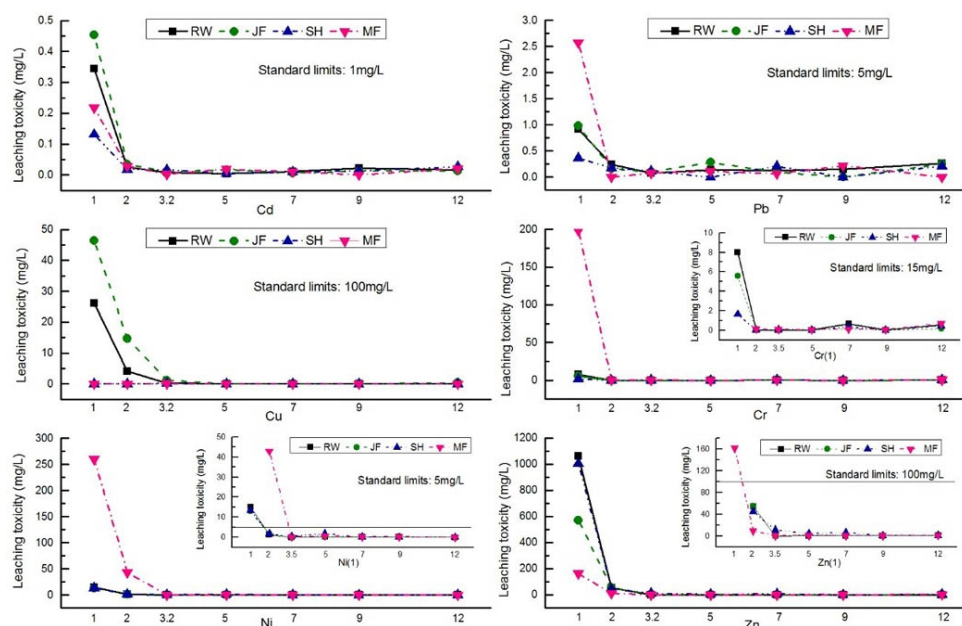

Fig. 4 Leaching toxicity of Cd, Pb, Cu, Cr, Ni, Zn in slag at different pH

At the same time, in order to investigate the relationship between the leaching toxicity and the element content in the slag at pH 1, pearson correlation analysis was carried out and the results are shown in Table 5.

Table 5. Correlation between leaching toxicity and content of slag at pH 1

	Cu	Cr	Ni	Zn	Cd	As	Ba	Pb	Se
Pearson Correlation	0.884	0.280	0.726*	0.364	0.171	-0.255	0.650*	0.148	0.800**
Sig. (2-tailed)	0.116	0.405	0.011	0.270	0.615	0.450	0.030	0.663	0.003

It can be seen from Table 5 that only the leaching toxicity and contents of Ni and Ba in the slag were positively correlated at the significance level of 0.05, with the strong correlation coefficients of 0.726 and 0.605 respectively. The leaching toxicity and content of Se in the slag was correlated at the significance level of 0.01, with the same strong correlation coefficients of 0.800, indicating the leaching toxicity of these three elements in the extreme acid environment was seriously affected by the contents in the slag and leaching toxicity increased with increasing metal content. In contrast, the correlation study of Cu did not show relationship between leaching toxicity and content of the metal. Compared with the leaching toxicity and the element content data, it was found that the Cu content was higher in RW slag than in JF, but the Cu leaching toxicity of RW's slag was smaller than the leaching toxicity of JF's slag. It is shown that the leaching toxicity of Cu at pH 1 was related to its element content in the slag, and the solidification effect. Although both RW and JF were copper-treated enterprises and the slag were naturally cooling, the slags obtained from the sludge at high temperature during the smelting process have a different solidified effect for heavy metals due to the additives and operating parameters.

Conclusions

The contents of Cr, As, Co in the slag after high temperature smelting were affected by their contents in the sludge, while others were affected by the process. Cu, Ni and Cd were removed by high temperature smelting, while Mn, Ba, Be Cr and Se showed a serious enrichment phenomenon.

The solidification effect of Cu, Ni and Cd was very significant, and good for Zn and Cr, while poor on Ba, which was mainly because of its high content in slag.

Natural cooling slag RW and JF formed more crystal structure, while the water quenching slag SH and MF appeared less in the crystal which had no advantage of solidification effect over the natural cooling slag, with only difference in structure. Surface of the slag disposal of copper sludge after high temperature smelting was dense, while there were various substances on the surface of electroplating and pickling sludge, most of which were different morphological materials.

As, Ba and Se did not appear excessive in different pH solutions. Cd, Pb, Cu, Cr, Ni and Zn were leached under acidic conditions, among which Cd, Pb and Cu did not exceed at all sites while Cr, Ni and Zn appeared excessive in some samples. The solidification effect of SH and MF on Cd was better than that of RW and JF; the solidification effect of slag on Pb was good under the condition of weak acid, but weakened under strong acid condition with an overflow of Pb; the leaching toxicity of Cu at pH 1 was related to its element content in the slag and the solidification effect.

In general, the solidification effect of heavy metals in slag produced from the sludge by high temperature smelting in the extreme acidic environment was poor while better in weak acid to alkaline environment. The removal and solidification of different metals and the same kind of metal in different enterprise samples due to additives and process parameters were also not the same.

Acknowledgements

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