Harmless Disposal and Comprehensive Recovery of Cadmium Waste Slag

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Abstract: According to the material characteristics of cadmium waste slag, it obtained oxide dust which were the preconcentration of cadmium and other metal by roasting. The best process parameters also was obtained through the test. Detoxicated slag was processed by grinding and magnetic separation. The iron grade of rich iron slag was 56.27% and the iron grade of the poor iron slag was 30.7%.

1. Introduction
Cadmium is an important raw material of the national economy, but it is also a serious toxic substances[1]. Smelting dust and slag is the major pollutant in the metallurgical production process, it is also often open yard. Due to the stacking area without any treatment, the dust and exudates has a greater impact on the surrounding ecological environment and groundwater after years of expose to the weather and rain. Therefore, it is necessary to do harmless treatment of these cadmium slag. Cadmium waste containing Cd, Ag, Zn, Cu, Fe and other metals. If we can recycle valuable elements in the process of harmless, it can turn waste into treasure, and achieve comprehensive recovery and utilization of resources, it also can increase the economic efficiency of enterprises[2].

At present, we are carrying out the strategy of sustainable development in China. The waste residue and waste gas of the smelter need to be reclaimed and utilized, it not only can effective reuse resources and protect environment, but also obtain high value-added chemical product.

2. Cadmium slag properties
The multi elemental analysis of the test sample was shown in table 1. It show that the main metal elements of the waste were iron, zinc, copper, cadmium and so on, X diffraction analysis show that the metal is mainly in the oxide form, and gangue is mainly composed of silica, calcium oxide, alumina and Magnesium Oxide and carbon. In addition, the silver content of the slag was 21g/t.

Table 1 chemical composition of cadmium waste slag

| Component | Fe  | Zn  | Cu  | Cd  | Ag  | Pb  | S   | C   | SiO₂ | CaO  | MgO  | Al₂O₃ | As  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|-----|
| Content (%)| 26.15| 3.2 | 0.31| 0.3 | 0.05| 0.50| 8.2 | 23.97| 12.24| 3.57 | 14.97| 0.28 |

The leaching toxicity test results of cadmium waste slag was shown in table 2. It shows that the cadmium slag belongs to toxic harmful dangerous waste solid, it is dangerous at the long-term storage, it must be harmless disposal.
Table 2  leaching toxicity results of cadmium waste slag (mg/l)

|                | The total Cr | Six valence chromium | The total Cu | The total Pb | The total Zn | The total Cd | The total As | PH |
|----------------|--------------|----------------------|--------------|--------------|--------------|--------------|--------------|-----|
| cadmium waste slag (acid leaching) | 1.504 | 0.030 | 3.695 | 1.902 | 37.960 | 2.2592 | 0.1831 | 3.98 |
| cadmium waste slag (water leaching) | 0.013 | ≤0.004 | 2.441 | 1.598 | 30.960 | 1.4560 | 0.1290 | 4.25 |

According to the material characteristics, we obtained oxide dust which were the preconcentration of cadmium and other metal by roasting. Rotary kiln slag is processed by grinding and weak magnetic separation, it finally realize the harmless treatment and comprehensive utilization of resources. The mixture of Cadmium waste slag and coal is fed into the kiln to roasting at high temperature. Cadmium is oxidized at high temperatures, the oxide is volatilized into the system of the flue gas cooling and dust recovery, recycling cadmium dust was the raw material of wet metallurgical production workshop; the cooling detoxification slag which was from rotary kiln was entered into the crushing and grinding system, When it is grinding to a certain fineness, the iron in slag can be separated and recovered by two sections of magnetic separation. The Water can be recycled in the magnetic separation process.

3. Study on the technological conditions

3.1 Roasting experiment

3.1.1 Effect of Temperature and volatilization rate of cadmium and zinc
When addition amount of lignite was 35%, a rotational speed of the kiln was 0.4r/min (the staying time of the materials in the kiln body is 3.5h), inlet amount of cadmium waste slag was 8kg/h. Change relationship of temperature and volatilization rate of cadmium & zinc was shown in Figure 1.

It shows that the volatilization rate of zinc and cadmium increases with the increase of temperature from Figure 1. When the temperature is higher than 1100 °C, cadmium zinc volatilization rate declined. Cadmium and zinc volatilization rates were 82.4% and 76.8% at 1100 °C.

3.1.2 Effects of coal proportioning and volatilization rate of cadmium and zinc
When addition amount of lignite was 35%, a rotational speed of the kiln was 0.4r/min, inlet amount of cadmium waste slag was 8kg/h. Effects of coal proportioning and volatilization rate of cadmium and zinc was shown in Figure 2 at 1100 °C. From the graph results, volatilization rate of zinc and cadmium increased with the increase of coal proportioning, the suitable coal proportioning was 35%.
Figure 1. Effect of Temperature and volatilization rate of cadmium and zinc.

Figure 2. Effects of coal proportioning and volatilization rate of cadmium and zinc.

Figure 3. Effects of inlet amount of cadmium waste slag and volatilization rate of cadmium and zinc.

3.1.3 Effects of inlet amount of cadmium waste slag and volatilization rate of cadmium and zinc
When addition amount of lignite was 35%, a rotational speed of the kiln was 0.4r/min, inlet amount of cadmium waste slag was 8kg/h, Effects of inlet amount of cadmium waste slag and volatilization rate of cadmium and zinc was shown in Figure 3 at 1100 °C. In the small inlet amount of cadmium waste slag, the volatilization rate of cadmium and zinc have better evaporation rate, when inlet amount of cadmium waste slag was greater than 8 kg/h, The volatilization rate of cadmium and zinc fall.

3.1.4 the component analysis of the dust and Kiln slag
We obtain the best process parameters through the test condition (the optimum temperature is 1100 °C, addition amount of lignite was 35%, staying time of the materials in the kiln body is 3.5h, inlet amount of cadmium waste slag was 8kg/h), we get a certain amount of oxide dust and slag under that condition, the yield of the two product were 10% and 84.4%, Multi element analysis results of the oxide dust and slag are shown in table 3 and table 4.
### Table 3 Chemical composition of the cadmium dust

| Component | Fe  | Zn  | Cu  | Cd  | Ag  | Pb  | C   | SiO₂ | CaO  | MgO  | Al₂O₃ |
|-----------|-----|-----|-----|-----|-----|-----|-----|------|------|------|-------|
| Content (%) | 12.75 | 24.10 | 1.23 | 2.51 | 0.38 | 5.32 | 2.12 | 3.63  | 2.04  | 4.49  |        |

We can know the zinc and cadmium in dust get effectively enrichment from table 3, The content of zinc, copper, cadmium and silver respectively were 24.1\%, 1.23\%, 2.51\% and 120g/t, Their recoveries were 77.03\%, 81\%, 40.03\% and 61\%.

### Table 4 Chemical composition of the slag

| Component | Fe  | Zn  | Cu  | Cd  | Ag  | Pb  | S   | SiO₂ | CaO  | MgO  | Al₂O₃ | As   |
|-----------|-----|-----|-----|-----|-----|-----|-----|------|------|------|-------|------|
| Content (%) | 29.05 | 0.8 | 0.21 | 0.006 | 9.5g/t | -  | -  | 6.2  | 27.35 | 12.39 | 3.90  | 17.27 |

We know that the kiln slag that cadmium content in the slag is 0.006\% from Table 4. The leaching toxicity test results of Detoxicated slag was shown in table 5.

Oxide dust can be sent to the system of the hydrometallurgical to recovery of useful metals, we can get the sponge cadmium products, it can achieve comprehensive recovery of valuable material and harmless disposal of cadmium waste slag.

### Table 5 The leaching toxicity test results of detoxicated slag(mg/l)

|                        | The total Cr | Six valence chromium | The total Cu | The total Pb | The total Zn | The total Cd | The total As | PH  |
|------------------------|--------------|-----------------------|--------------|--------------|--------------|--------------|--------------|-----|
| Cadmium waste slag     | ≤0.004       | ≤0.004                | ≤0.02        | ≤0.1         | 0.006        | ≤0.005       | 0.0273       | 7.47 |
| (acid leaching)        |              |                       |              |              |              |              |              |      |
| Cadmium waste slag     | ≤0.004       | ≤0.004                | ≤0.02        | ≤0.1         | ≤0.005       | ≤0.005       | 0.0235       | 8.69 |
| (water leaching)       |              |                       |              |              |              |              |              |      |

3.2 Magnetic separation test of detoxicated slag

It shows iron grade of detoxicating slag was 28.86\% in table 4. A portion of the iron compounds were converted to magnetic iron after calcinations. It can be considered that we can get Part of rich iron products as iron concentrate by magnetic separation, it can achieve the aim of comprehensive utilization.

Detoxification slag was grinded to a fineness of -0.074mm accounted for 60\%, we obtain coarse concentrate after a weak magnetic separation (0.25T), Coarse concentrate was regrinded to -0.074mm accounted for 85\%, we get rich iron slag after two period of weak magnetic separation (0.15T), The tailings was low iron slag. multi element analysis results of the rich iron slag and low iron slag were shown in table 6 and table 7.

It shows that the iron grade of rich iron slag can reach 56.27\% in table 6, it can be considered to use as raw material for puddling. The yield of rich iron slag was 30.7\%, the iron recovery rate was 67.69\%. The yield of low iron slag was 53.7\%, low iron slag can be considered as the building materials. Table 7 show that cadmium content in the slag is 0.005\%, it was the detoxicated slag, detoxification slag was the General solid waste slag, it can be storage and reused.
Table 6 Chemical composition of high iron slag

| Component | Fe   | Zn   | Cu   | Cd   | Ag   | Pb   | SiO₂ | CaO | MgO | Al₂O₃ |
|-----------|------|------|------|------|------|------|------|-----|-----|-------|
| Content (%) | 56.27 | 0.29 | 0.16 | 0.005 | 40g/t | 2.0  | 22.21| 9.30 | 4.27 | 12.69 |

Table 7 Chemical composition of low iron slag

| Component | Fe   | Zn   | Cu   | Cd   | Ag   | Pb   | SiO₂ | CaO | MgO | Al₂O₃ |
|-----------|------|------|------|------|------|------|------|-----|-----|-------|
| Content (%) | 12.97 | 1.08 | 0.23 | 0.005 | -    | 0.001| 8.89 | 31.782| 13.98| 3.59  | 19.57 |

4. Conclusion
(1) It obtain the best process parameters through the test condition (the optimum temperature is 1100 ℃, addition amount of lignite was 35%, staying time of the materials in the kiln body is 3.5h, inlet amount of cadmium waste slag was 8kg/h). the kiln slag that cadmium content in the slag is 0.005% was detoxicated slag, detoxification slag was the General solid waste slag, it can be storage and reused.
(2) It get a certain amount of oxide dust and slag under the most suitable condition, the yield of the two product were 10% and 84.4%, the zinc and cadmium in dust get effectively enrichment, The content of zinc, copper, cadmium and silver respectively were 23.8%, 1.21%, 2.46% and 120g/t, Their recoveries were 77.03%, 81%, 40.03% and 61%.
(3) The detoxicated slag be processed by grinding and magnetic separation, We have rich iron slag that its iron grade can reach 56.27% and poor iron slag that its iron grade can reach 30.7%. The yield of rich iron slag was 53.7%, low iron slag can be considered as the building materials.

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Reference:
[1] Gaballah I, Kanari N. Recycling Policy in the European Union[J] JOM. 2001. (11): 24-27.
[2] SHAO Qiong, DU Xia, WANG Ling, L AN Rao-zhong. Present Status of Reutilization of Copper-cadmium Slag[J] Hydrometallurgy of China Vo1.22 No.2(Sum.86) Jun.2003 66-68