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Industrial experiment on heavy metal recovery of stainless steel slag

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Abstract

Industrial experiments on the hydrometallurgical recovery of heavy metals were carried out to identify ways to prevent heavy metal leaching from stainless steel tail slag and provide a scientific basis for producing steel slag fertilizers. The results showed that the comprehensive recovery percentages for metals could reach up to 86% to 95% with the process described in this paper. The average recovery percentages for Cr and Ni were about 90%. The experimental research results have been applied to engineering, and good results have been achieved. Based on mineralogical phase components of heavy metals and separation mechanisms, technological characteristics and influencing factors of the process were analyzed, and techniques for debugging are described herein. All the results should provide a good reference for widespread applications of the process.

Keywords: Stainless steel slag,Heavy metals,Industrial experiment

1. Introduction

This According to statistics in 2021 China's stainless steel production of more than 32 million tons. The total amount of steel slag about 8.5 million tons. Most of the current stainless steel slag utilization in China is only a simple metal particle recovery of the original slag. the tailing slag is abandoned in large quantities. Most of the stainless steel slag after crushing and dry sorting slag steel reuse. The remaining 0~10mm tailings are not used. These tailings still contain more heavy metals than the standard allows. Without steady-state treatment, the Cr compounds in it can dissolve highly toxic Cr^{6+}, which endangers the environment and human safety[1-2]. The depth of its treatment will not only achieve significant economic and social benefits, but also has a strong demonstration role.

The tailings are porous, with large surface area and good adsorption. It contains a large amount of calcium, magnesium, silicon and other elements that are beneficial to crops and soil. It can be applied to agriculture and soil improvement on a large scale[3]. However, the prerequisite for utilization is that the heavy metal content of the soil after application should comply with the Standard Value of Land Pollution Technical Provisions. The tailings are treated to have the lowest possible content of heavy metals in them.

According to the United States stainless steel slag fertilizer production experience. When the metal content in the slag is below 1‰, most of the toxic heavy metals that can undergo leaching can be removed. The fertilizer produced can meet the U.S. standard for agricultural applications of steel slag. If the production is to achieve these goals, then the removal rate of all metals from the tailings has to be more than 95%. In addition, for the plant to achieve commercial operation on a large scale, the recovered metal grade should be above 80%. The requirement to achieve such a high recovery rate and metal grade at the same time is very difficult.

2. Technology Status in China

Stainless steel slag metal recovery in China is divided into wet and dry methods. The wet method is represented by the electric furnace slag and refining furnace slag processing line of Shanghai Baosteel Group. The steel slag is crushed and then selected by jigging process for slag steel above 7 mm [4] (grade ≥ 85%). The dry method is represented by the electric furnace slag processing line of Taiyuan Stainless Co. Ltd. It applies metal induction separator and strong magnetic separator to recover the crushed lumpy metallic material (particle size ≥ 15 mm).

The above methods are mainly for flake and granular monomeric metals in slag. These larger monomeric metals encapsulated in the slag are easily dissociated under external forces. Metal particles meeting the commercial sales requirements have a diameter of 3mm or more. The recovery rate and grade are very unsatisfactory for metal particles below the millimeter level that exist in a fine mesh vein-like embedded state.

3. Steel slag characteristics

Stainless steel slag from a large stainless steel company in Shanxi Province was used as a raw material for industrial tests.

The stainless steel production of the company. adopted the "electric furnace - converter" and "primary furnace - top bottom blowing converter - vacuum refining furnace" process respectively [5]. The nature of the stainless steel slag produced by different processes and procedures varies. From the physical form, natural cooling electric furnace slag is generally dark lumpy. It is locally visible metal mosaic distribution. Refinery slag and converter slag is usually beige in color and has very little metal content. It is easily crushed during cooling and ends up in a granular or powdered form. The main mineral composition of stainless steel slag is dicalcium silicate. Some of them are chrome spinel, calcium chromite, calcium ferrite, metallic iron chromium nickel, etc. Among them, calcium chromate is highly toxic [6].

The stainless steel slag used as raw material for the test is mainly electric furnace slag, refining furnace slag, converter slag after dry sorting of mixed slag. 80% or more particle size less than 5 mm. the chemical composition of the slag is as follows: CaO is 48%, SiO_2 is 24%, Al_2O_3 is 13%, MgO is 5.4%, NiO is 0.38%, Cr_2O_3 is 1.2%, TFe is 2.4%.

4. Industrial trials

To prepare for the construction of 1 million t/a tailings treatment line. The industrial test team transported the stainless steel tailings and a certain percentage of raw slag to a small production line in the United States. Conducted a "two-stage grinding, two-stage sorting" steel slag treatment process industrial trials.

Under the condition that the material is all tailings, the feed and grinding product sieve analysis data are shown in Tables 1 and 2. The metal recovery rate and grade test data of each unit process are shown in Table 3. According to the design hourly capacity, the φ3.6m×5.4m rod mill is adopted for one section grinding and the φ3.2m×5.4m ball mill is adopted for the second section grinding.

***Table 1.**Grain size analysis of input tail slag*

Mesh	Screen size (mm)	Grader retained (%)	Oversize cumulative (%)	Undersize cumulative (%)
	4.75	7.48	21.43	78.57
8	2.36	2.76	24.18	75.57
16	1.18	2.98	27.16	72.84
20	0.85	1.61	28.77	71.23
30	0.6	1.93	30.71	69.29
50	0.3	6.40	37.11	62.89
100	0.15	10.04	47.14	52.86
200	0.075	16.60	63.75	36.25
Sieve bottom	0	36.25	100	0

***Table 2.**Grain size analysis of ball mill outlet*

Mesh	Screen size (mm)	Grader retained (%)	Oversize cumulative (%)	Undersize cumulative (%)
30	0.6	0	0	100
50	0.3	0.65	0.75	99.25
100	0.15	7.85	8.32	91.68
200	0.075	20.41	28.73	71.27
Sieve bottom	0	71.27	100	0

***Table 3.**Separation technology index* （%）

Product name	Yield	Grade	Metal recovery
Primary spiral sorter	6.85	37.12	84.54
Secondary spiral sorter	2.87	88.43	84.27
Primary magnetic separator	4.71	15.40	24.18
Secondary magnetic separator	2.03	32.06	21.33
Triple spiral sorter	0.91	38.78	11.63

The tailings after the second grinding and iron removal are dewatered by vacuum and dried naturally. Then sample division was performed. The specimens were configured into different concentrations and several sets of natural settling tests were performed. One of the typical settlement curves is shown in Figure 1. the specification of the thickener was determined to be φ30m according to the treatment capacity and settling data (aggregate settling speed 4.7mm/min).

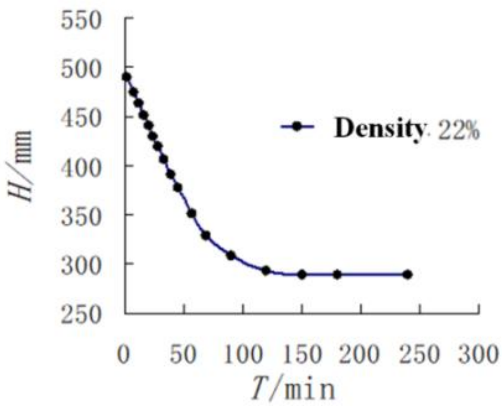

***Figure 1.** Subsidence curve of ore pulp*

The filtration and dewatering of tailings after metal recovery was carried out using a “four-factor, three-level orthogonal analysis experimental method”. The effects of filter cloth variety, filter speed, vacuum, and feed concentration on the filter cake yield and water content were determined. The data used for the design are presented in Table 4. two disc vacuum filtration machines were selected based on the amount of slurry to be filtered and the test output per unit area. They have a filtration area of 96 m2 and a diameter of 2.8 m. Parameters such as the range of filtration speeds, the distribution ratio between the filtration and drying zones, and the height at which the material is unloaded by backblowing are also determined.

Table 4. Dewatering assay of tail slag

Rotationaltime (rpm)	**Filtration time (s)**	**Drying time (s)**	**Filter cake**	**Water content**	**Gapacity (Kg/h.m^2)**
0.5	39	48	10.5	20.2	421.4
1	20	24	8	20.6	628.2
1.5	13	16	7.5	21.0	896.4

Experimental conditions: Feed concentration 45%, Filter cloth weight 600g/m2, Vacuum Level -0.06MPa.

The above industrial test data were integrated. Full process stainless steel slag material and water balance calculations were performed. A design basis is provided for practical engineering applications.

5. Industrial trials

5.1. Process Flow

The raw material is mainly tailing slag, while raw slag or mixed slag can also be processed. The processing line includes a crushing system, grinding and sorting system. The crushing system crushes the raw slag to a particle size of less than 100 mm. Then it feeds the grinding and sorting system, and large pieces of scrap are selected manually. The production line is operated on a one-shift basis. The production line is built outdoors. The production process is shown in Figure 2.

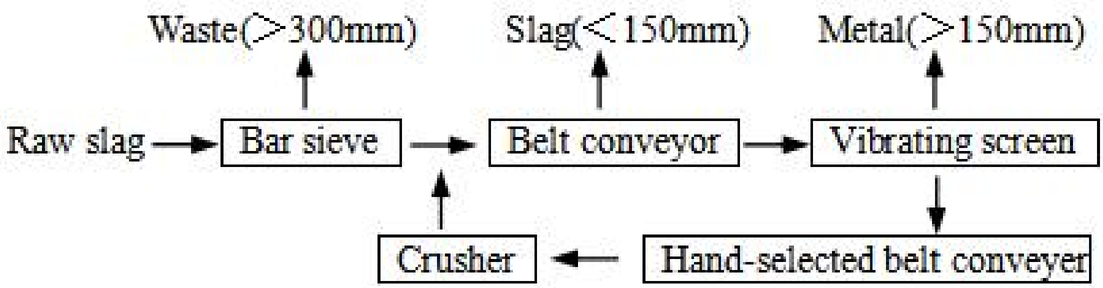

Figure 2. *Crushing circuit*

The grinding and sorting system is two lines with the same capacity (2×110 tons/hour). It operates in three shifts. The two production lines are being built in the same large factory building. In order to run smoothly in winter, the plant is equipped with heating and insulation facilities. The dewatered tailings are stored in a special plant as raw material for fertilizer production. The dewatered tailings are stored in another plant as raw material for fertilizer production, and are dried and used to make silica fertilizer. The production process is shown in Figure 3.

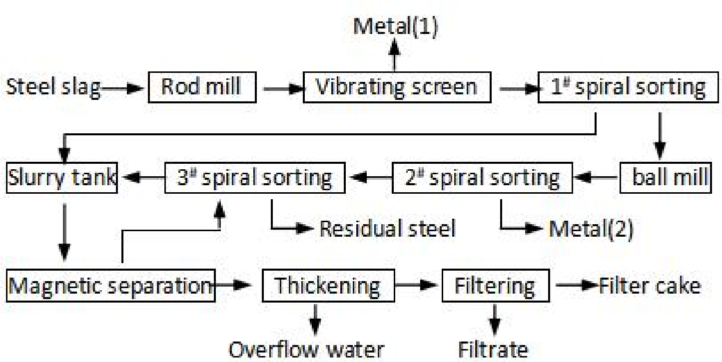

Figure 3. *Grinding and classification circuit*

Steel slag smaller than 100 mm is ground by the rod mill to less than 0.5 mm and enters the primary spiral classifier. The large particles of metal (1) that cannot be ground are collected together on a vibrating screen. Then it is dewatered and recovered. Their metal grade can reach more than 98%. The materials with particle size less than 100µm in the primary spiral classifier overflow into the slurry tank in the form of slurry. The rest goes to the ball mill for further grinding. 60% of the steel slag is ground to less than 75 µm. then the metallic material(2) is selected through a second spiral classifier. The overflow enters the third spiral classifier.

The overflow from the first and third classifier is pumped to the magnetic separator for de-ironing. After magnetic separation the steel slag is enriched with metals. They are again returned to the three classifiers for sorting. The magnetic separation tail slurry flows into the thickener for settling. The concentrated bottom stream with a concentration of 45% to 55% is pumped into a disc filter machine for processing. The resulting filter cake has a moisture content of less than 22%. The overflow from the thickener flows into the process tank as recirculating water.

5.2. Operational debugging

Depending on commercial operational requirements, a certain percentage of raw steel slag is sometimes mixed into the feed. This can result in large variations in the feed characteristics of the grinding and sorting system. Frequent adjustments of the system process parameters became the norm. The main operating parameter adjustment points are as follows:

The grinding concentration and discharge size of the rod mill. This can be controlled by adding water and adjusting the number of steel rods.

Overflow concentration of primary spiral sorting. Controlled by the height of the overflow weir and the amount of water added.

Ball mill discharge size. Adjust the amount of feed and the amount of steel balls added to control.

Washing intensity and time during secondary spiral sorting. Adjusted by rinse water pressure, water volume and classifier speed.

Concentration of the bottom flow in the thickening tank. Adjusted by the flow rate of the bottom flow pump.

The water content of the filter cake of the disc filter. Controlled by feed concentration and filter disc rotation speed.

The above adjustments are closely related to metal recovery and grade. A change in one parameter often causes a series of subsequent changes. During the commissioning process the grade of the main product metal(2) fluctuated in the range of 60% to 94%. The corresponding market price fluctuations also reached 50%. When adjusting to maintain the stable operation of the production line, special attention should be paid to keep the material and water system in balance.

5.3. Project operation results

The project took a total of 11 months from construction to commissioning. The process parameters of each unit were adjusted according to the industrial test data, and finally the design indexes were achieved. The total investment of the project is USD 16.45 million. The total installed power is 4,800kW, the area is 23,000m2, the construction area is 6， 000m2, and the production line has 42 employees. The water consumption is 0.3 m3/ton. The electricity consumption per ton of stainless steel slag is 16.3 kW.h. The overall cost of metal recovery is US$ 387. The economic return of the project is very good. Based on the recovered metal (grade 85%) selling price of 970~1290USD. The project investment can be recovered in less than 3 years. The tailings after metal recovery can be made into silica fertilizer after drying, blending and granulation. Part of it is exported to the United States and part is used in China.

The production line can produce the following three types of metal products that can be sold.
The production line can produce the following three types of metal products that can be sold.
(a) metal (1); (b) metal (2); (c) Residual steel. Six years later, the line is still running very well. The attached Figure 4 shows the appearance of the three products.

(a) （b） (c)

Figure 4. *Three kinds of metal products*

6. Process Characteristics Analysis

This project is the world's largest stainless steel slag metal recovery production line. It integrates American and Chinese technologies in the grinding, sorting, magnetic separation, and concentration and dewatering processes. Finally a unique set of process flow is formed.

(1) Compared with the dry method, it is suitable for all sizes of stainless steel slag. The dry process uses mainly metal inductors and magnetic separation equipment. Austenitic and ferritic steels are recovered separately. Induction sorting is effective for feedstocks with particle sizes over 15 mm. Although strong magnetic separation equipment can be used for finer materials, but because the particles can not be uniformly dispersed in aqueous solution. They cannot be repeatedly tumbled and rinsed on the surface of a magnetic separation drum with alternating polarity. The final result is a low grade of recovered material metal.

(2) China's domestic wet process technology mainly follows the magnetite beneficiation process. The process design follows the principle of "stage grinding, stage separation". Low-grade difficult-to-sort minerals are discarded with the process section by section. This design idea is suitable for natural minerals containing about 30% iron. But stainless steel tailings metal content of only 2% to 3%. It belongs to the very poor "man-made ore". Precious metals Ni, Gr content is even lower. Lower recovery rate means a significant increase in unit operating costs. This is also the reason why the domestic wet process does not take the low metal content of the refining furnace, converter slag as the main object of treatment. With this technology the raw material can be fed completely into the mill. The main product is selected in a single pass in the secondary classifier. Although the size of the mill increases, the process is greatly reduced. This method creates conditions for maximizing recovery rates.

(3) Although this technology is similar to the Chinese domestic "two-stage mill" beneficiation process. However, the role of the first stage mill is significantly different. In the beneficiation process, the first stage mill is mainly set up to reduce the workload of the second stage mill for stage separation. For the first stage mill with defined specifications, it is desired to minimize the discharge size while maintaining capacity. However, the one-stage rod mill in this project only has a higher output when processing raw slag and mixed slag. Under the condition that the feed is all tailings, as the production is mainly gravity separation. It is difficult to precipitate the overfine metal compounds quickly at a predetermined time and concentration. They will be lost with the overflow. Therefore, the

discharge size of the rod mill must be controlled and not too small.

(4) The design of the separation process is such that jigging and shaking table processes are mainly used for domestic wet technology in China. This project abandoned this traditional design. The spiral classifier, which is rarely used in the main separation process, was adopted. The metals in the tailings are mainly embedded in spherical grains. A few of them are filled inside the slag in the form of speckled flakes. The particle size generally ranges from 0.01 to 0.50 mm, with a few sizes of 0.60 to 0.90 mm [8]. The jigger is used as a medium grain re-election equipment. In practice, the lower limit of the sorting particle size around 1 mm is more effective [9]. The sorting effect is very poor for micron-sized particles. The shaking table sorting particle size range is large, but the single unit capacity is too low. The sinking spiral classifier adapts exactly to the embedded characteristics of the metals in the tailings in the classification particle size range. The single-unit capacity can also meet the design requirements. The application should be designed according to the industrial test data on the spiral blade, central shaft, trough body and other structural parameters.

(5) The tailings used for the production of silica fertilizer have strict requirements for heavy metal content. The leachable chromium content measured in the filter cake leaching experiment was 0.099 mg/L. No leached Cr6+ value was detected. This index is less than the U.S. waste leachable chromium standard of 5 mg/L, and even less than the Chinese standard value [9-10]. According to the X-ray diffraction pattern [11]. The main forms of Gr and Ni present in the Stainless steel slag are MgCr2O4, (Cr, Al)2O3, Gr2O3, and Ni-Cr-Fe metals. Among them Gr2O3 is insoluble in water. Cr-Fe (Ni-Cr-Fe) has strong magnetic properties, and the rest have weak magnetic properties. The project is a segmentation sorting process with specific gravity difference and magnetism as the removal mechanism. It is well suited to the physical phase characteristics of heavy metals in the tailings.

The main purpose of the magnetic separation process is not to recover, but to minimize the metal content of the slag. It requires high magnetic field strength and magnetic field gradient [12]. The design used a two-stage tandem counter-current magnetic separator. The magnetic field strength at 50 mm from the surface of the barrel is 95 mT. However, this is a necessary step to ensure that the process of fertilizer production does not exceed the standard heavy metal content. This part of the recovered material can still be sold after further purification through the flotation process. Due to engineering investment constraints, this project did not proceed with its purification.

7. Analysis of operational problems

Two-stage grinding and sorting process in the design and commissioning operation process to pay attention to design details. Designers should pay special attention to the impact of some unique physicochemical properties of stainless steel slag on the structure, equipment and production process. Improper handling can seriously affect the stable operation of production.

(1) Heavy metal pollution prevention problems. Cr^{3+} has the potential to be oxidized to Cr^{6+} under room temperature conditions in the presence of CaO [13-14]. The oxidation rate is closely related to the material size, solution pH, and time [15]. The engineering design of the thickener, process pond, and drainage ditch should take a variety of waterproofing measures. For example, the inner wall is coated with multiple layers of polymeric waterproofing mortar. Increase the grade and thickness of concrete impermeability. The outer wall uses a double layer of waterproof felt, etc. Workshops, material yard ground should also take anti-aging impermeable membrane. Production line in the steel slag sieving process, also added to prepare a solid reducing agent $FeSO_4$[16]. from time to time in the proportion of 2% into the raw materials. The purpose is to induce the reduction of Cr^{6+} to Cr^{3+}. The project has been monitoring the heavy metal content of groundwater within a 100 meter radius from the production line on a monthly basis since production began.

(2) The impact of material viscosity on production. Stainless steel tailing slag is basically in powder form. New slag moisture content of 10-15%. Natural accumulation angle is above 70º. Its fluidity is very poor. Coupled with its inherent alkalinity, it is easy to cause blockage of rod mill inlet during production. Equipment and pipe scaling. Large amounts of sticky material in the belt conveyor. In winter, it can cause production to stop in severe cases. There should be sufficient countermeasures in the design of devices such as mill inlet guide, belt machine scraping and filter discharge.

(3) Water balance control problem. System long-term operation, CaO in the material will make the pH value of circulating water rise significantly. Once the water system loses balance, the discharged wastewater will cause serious secondary pollution. If a large-scale wastewater treatment system is built, it will make the operation cost rise sharply. Due to transportation reasons, steel slag treatment facilities are generally built near the steel mill. It is not possible to build tailings dams with huge water balance regulation capacity. This requires a design that separates clear and turbid water for production and recycling as much

as possible. Water-saving equipment is also used to reduce the amount of new water. During the production trial run, the disk vacuum filtration machine was replaced with a more water-efficient ceramic vacuum filtration machine. This approach greatly reduces the difficulty of water balance control and improves the system operation rate. It is proved that the wet treatment can completely achieve zero waste water discharge.

(4) Concentration control issues for the overflow water from the thickener. This project was designed to minimize the amount of new water used. The rinsing of the recovered metals and the unloading of the material from the magnetic separator all use water from the overflow of the thickener. This approach requires the overflow water turbidity as low as possible. However, the number of suspended particles in a critical settling state during operation accumulates in a continuous cycle. In severe cases, the thickener will lose its clarification interface. The turbidity of the overflow water deteriorates rapidly. A large amount of ash is mixed into the recovered metal with the slag wash water. This causes a significant drop in grade. In this case, it is necessary to add alkaline polymer flocculant in the thickening pool. The amount of flocculant should be strictly controlled when adding. The purpose is to prevent the slurry from settling too quickly and pressing the rake at the bottom of the thickener. If this happens, it will be a serious operational accident. It will take at least two weeks for workers to resume production runs.

8. Conclusion

(1) Two-stage grinding and sorting process on the basis of industrial tests. Based on the embedding particle size and embedding characteristics of different heavy metal mineral phases in stainless steel slag. It can give full play to the advantages of strong processing capacity of rod mill and less over-crushing of slag particles. Realize the dissociation of single metal particles. The dissociation of microfine metal oxides is realized by taking advantage of the fine grinding products of ball mill. According to the different heavy metal mineral phase magnetic and density physical property difference, respectively, the spiral classifier and magnetic separator are used for targeted separation. The recovery rate and grade of heavy metals are ensured to the maximum extent. The grade of industrial production main product metal (2) is stable above 86%. The comprehensive metal recovery rate reached 95%. The production determination of Gr and Ni comprehensive recovery rate is 87% to 93%.

(2) The application of the process can balance social and economic benefits. It creates conditions for further large-scale agricultural utilization of tailings. The industrialization and promotion of application is of great value. The actual application should pay attention to the material and water system balance to prevent secondary wastewater pollution.

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