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Technological progress on detoxification and comprehensive utilization of chromium-containing slag ①

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[Abstract] Chromium salt is an important industrial material, but vast waste slag containing chrome(Ⅵ) is brought out in the process of its production. The slag is seriously harmful to environments and human health. The technologies on detoxification and comprehensive utilization of chromium-containing slag were summarized abroad and at home. And various methods were also described for the detoxification mechanism, technology process, and practical application effects in detail. A new concept for detoxification of chromium-containing slag, furthermore, was put forward by using microorganism.

[Key words] chromium-containing slag; detoxification; comprehensive utilization; microorganism
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1 INTRODUCTION

Recently some industries using chromium compounds, such as electroplating, chemistry, printing, dyeing and leather industry, have made good benefits, which promotes the scale-production of chromium salt plant and makes environmental problems worse[1, 2].

The Cr(Ⅵ) ion in chromium-containing waste water and waste slag yielded in producing chromium salts are harmful to person, crop, livestock. It not only has stimulation acts but also can induce pathologic change with being absorbed by stomach and intestines, resulting in asphyxia. Therefore, the Cr(Ⅵ) is a kind of carcinogenic substance, also one of 129 chief pollutants recognized by EPA in US. The sewage containing Cr(Ⅵ) will poison underground water, soil and the earth's surface, because rain washes the slag and then bring the dissolved Cr into the soil. At present, studies on chromium-containing wastewater in electric plating are paid wide attention, however, an efficient method has seldom been found for treating the slag. In the developed countries, the amount of the discharged slag and remained chromium in the slag was reduced with the improvement of the technology for producing chromium. It is early in the 1960's that the study was carried out for disposing chromium-containing slag at home. And some prosperous ways had been found, however, these methods still exist some shortcoming including bad effects of detoxification, complex apparatus, more investment, high operating cost and second dust pollution etc. Therefore, this paper is aimed at putting forward a novel concept for detoxifying and reutilizing chromium-containing slag, with discussing present studies.

2 ORIGIN AND COMPOSITION OF CHROMIUM-CONTAINING SLAG

The slag is mainly solid waste from the production of chromium salt, which is formed by calcining the mixture of calcined soda, dolomite, limestone and chromite at 1 100~ 1 200 ℃ and by leaching the sodium chromate. It is estimated that about 3~ 5 t chromium-containing slag will be produced to obtain 1 t chromate. The slag increases at 10^5 t annually, and the heaped amount in past years has exceeded 2.5×10^6 t since producing chromium salt in 1958 in China[3].

The composition of chromium-containing slag is presented in Table 1[4].

It can be found from Table 1 that the slag includes periclase (MgO) 20%, dicalcium silicate (β-$2CaO \cdot SiO_2$) 25%, calcium ferric aluminate ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) 25%, calcium chromite($\alpha$-$Ca(CrO_2)_2$) 5% ~ 10%, sodium chrome-spinel brick ($(MgFe)(CrO_2)_2$) 5% ~ 10%, calcium chromate($CaCrO_4$) 1%, sodium chromate containing four water ($Na_2CrO_4 \cdot 4H_2O$) 2% ~ 4%, and $3CaO \cdot Al_2O_3 \cdot 6H_2O$ 1%. The main constituents are almost the same as that of cement, the slag shows obvious hydraulicity, with hygroscopically caking in the air. Therefore, the slag is a remarkable architecture material, only if there exists no toxicity of Cr(Ⅵ) in it.

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Table 1 Constituents of chromium-containing slag (%)

Sample No.	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Total Cr	Total Cr^{6+}	Dissoluble Cr^{6+} in water	Dissoluble Cr^{6+} in acid	H_2O
1	8~ 11	5~ 6	9~ 11	29~ 3	19~ 27	3~ 7	2~ 4	1~ 3	< 2	—
2	9~ 10	5~ 6	11~ 12	3	20~ 30	2~ 3	—	—	—	—
3	6.79	5.12	11.35	30~ 50	28.44	5.53	1.11	—	—	14.3~ 19.25

However, the total Cr^{6+} ions including dissoluble Cr^{6+} in water and in acid occupy 2%~ 4% by mass in the slag, which is of strong toxicity.

So, the detoxification of Cr(Ⅵ) is of great importance to the slag before its reutilization.

3 DETOXIFICATIONN AND COMPREHENSIVE UTILIZATION OF SLAG

Chemical methods, in general, are adopted to detoxify the slag by changing Cr(Ⅵ) to Cr(Ⅲ), for getting rid of the hazard to the environment[5, 6]. In American, the slag is heaped together; however in Japan, Russia and Romania, it is utilized to manufacture aggregate and refractory material by pyro-based reduction method[7]. Another method, hydro-based reduction detoxification is also adopted in practice. The detoxified slag, and then, can be used as colorant-agent in making glass, additive in manufacturing calcium-magnesia phosphate fertilizer, flux in smelting iron, cast stone, man-made bone powder and chromium-cotton porcelain.

3.1 Detoxification and reutilization by pyro-based reduction[8~ 13]

3.1.1 Pyro-based reduction using coal powder

The blend are added into a rotary kiln with the mass proportion of coal powder to slag being 15/100, and the temperature being controlled above 290 ℃ at the tail of kiln, between 540~ 640 ℃ at the elevated thermal zone, between 740~ 840 ℃ at the discharged exit. The reaction materials stay in the elevated thermal zone for 8~ 10 min and in the kiln for 30 min, resulting in a good effect for detoxification. A total amount of 230~ 250 kg coal (among 100 kg as fuel, balance as raw material) is needed for treating 1 t slag. After the treated slag is remained above 45 d and insolated for c.a. 56.5 h, the content of Cr(Ⅵ) in the slag is not beyond 5 mg/kg. The technology has advantages of short flowsheet, simple equipments and lower operation cost, but with disadvantages of stricted operation conditions and bad detoxification effects. Except for using coal as reducing agent, some carboniferous solid wastes, including used activated carbon, sawmill scraps, sulfite liquor, rice husks etc, can also be applied as the reductant to reduce Cr(Ⅵ) at 200~ 900 ℃.

3.1.2 Burning of slag attached in cyclone kiln

Burning of slag attached in a cyclone kiln is a new dry-reduction technology for detoxification of the slag, developed in the middle of 1980's. In fact, it is also an improved technique based on the reduction of coal powder. Because cyclone kiln is provided with a great calorific intensity and an elevated temperature, coal can burn completely at low air-overplus coefficient, resulting in the reduction of Cr(Ⅵ) to Cr(Ⅲ) easily. With crush, mix of the slag and coal, chromium ion (Cr(Ⅵ)) is reduced with the slag being moltened, while air is sent into the kiln.

Because cyclone kiln has the advantage of dealing with large matter stream by combination of thermal and electrical applications, a large scale of chromium-containing slag can be treated. And the burned slag, furthermore, substitutes limestone to be flux. Thus, the technology needs hardly additional energy to detoxify the slag. An important problem, however, is still paid attention, which are concerned with the reduced slag being re-oxidized again, i.e. Cr(Ⅲ) being turned to Cr(Ⅵ).

3.1.3 Yielding cast stone with chromium-containing slag

The simulated cast stone is obtained with the raw materials which are composed of 30% slag, 25% silicon sand, 45% fuel dust, and 3% ~ 5% iron sheet, being mixed, crushed, moltened at 1500 ℃, cast-formed at 1300 ℃, recrystallized and annealed. The product is an excellent material for resisting acid and corrosion. The method can get fine purpose but is restricted for application, because of no wide market demands for cast stone also greater investment, a large occupied space for production.

3.1.4 Substitution of serpentine for producing calcium-magnesium phosphate fertilizer

It can be known that the slag contains high contents of MgO, SiO_2, showing it can be used to produce calcium-magnesium phosphate fertilizer in place of serpentine, in which main components are MgO and SiO_2. Firstly, the mixture with the mass proportion of anthracite: phosphate: slag: silica being 37.5: 50: 35: 15 is used to produce pellet and then the product is formed by melting the pellet at 1 600 ℃, water quenching, separating, drying in a rotary drum and crushing. This method consumes a large quantity of chromium-containing slag, and receives good detoxification effects. However, it requires much money, large production site and more fuel to elevate temperature.

3.1.5 Substitution of dolomite and limestone for smelting iron

The contents of CaO and MgO in the slag are also close to those of dolomite and limestone, so it can be used for smelting iron. To obtain 1 t pig iron, 600 kg chromium-containing slag will be consumed. By this method a large number of chromium-containing slag can be disposed and Cr(Ⅵ) can be detoxified completely. The properties of iron including mechanical character, hardness, wear and corrosion-resistance are improved with the increase of chromium. Therefore, it is a perfect approach for detoxification and comprehensive utilization of chromium-containing slag. The secondary pollution, however, must be avoided in the process of transportation, storage, comminuting, pelletization and sintering.

3.1.6 Producing artificial bone material

The mini-scale experiment for producing artificial bone material was done by Jinan Yuxing Chemical Plant and Shandong New Material Institute in 1983, and the pilot experiment was done in 1986.

The mixture of chromium-containing slag, the yellow river beach soil and coal ash is crushed, formed and calcined to produce artificial bone material. There exists 5×10^{-8} g water-soluble Cr(Ⅵ) per each kg product, which passed all tests in properties. The technology can detoxify the slag completely, and the raw materials are of low price and easily obtained, with wide commercial popularity. The great energy consumption of and small demand of production block, however, limit the extended utilization of the technology.

3.1.7 Substitution of chrome ore for producing glass colorant

Generally, chrome ore powder was used to produce green glass since Cr(Ⅲ) can absorb lights with wave lengths of 446~461 nm, 656~658 nm and 684~688 nm while permeate others. Infrared ray absorption band appears around 650~680 nm and blue absorption band appears near 450 nm. When the two bands combines, the glass looks green. The chromium-containing slag contains some remaining chrome ore powder and Cr(Ⅵ) which can be changed to Cr(Ⅲ) after being heated. So it can be the substituent of chrome ore powder for producing glass colorant.

At present, many factories have made use of chromium-containing slag instead of chrome ore powder to produce glass colorant in Tianjin, Qingdao and Beijing. The advantages of this method include that Cr(Ⅵ) can be reduced to Cr(Ⅲ), which realizes the goal of detoxification, the MgO and CaO in the slag can substitute dolomite and limestone in glass dosage, which decreases the cost, the glass possesses fresh color and high quality. The glass appears green, emerald and bottle green, respectively when the addition of the slag is up to 2%, 3%~5% and 6%. The addition amount cannot exceed too much, otherwise, the glass will be opaque. For a little demand to green glass, this method merely deals with too little chromium-containing slag.

3.2 Detoxification and reutilization by hydro-based reduction

3.2.1 Hydro-based detoxification by reducing agent[14]

The chromium-containing slag is wet-ground to a paste of 0.124 μm in slag powder grain and was put into detoxification reactor, and then heated to 90 ℃, followed by the addition of 15% Na_2S solution. With the reaction for 30 min, pH is adjusted to 7~8 by adding sulfuric acid. The 20% FeSO4 solution is added to the mixture. After treatment, the solution is transparent and colorless, and the content of Cr(Ⅵ) is less than 0.5×10^{-6} g/g. The filtered residue contains Cr(Ⅵ) less than 108×10^{-6} g/g and stacked.

In addition, NaHS, $FeSO_4$ or Na_2SO_3 can also be selected as reducing agents besides Na_2S. This treatment can not remove toxicity completely, and is expensive in cost. Furthermore, excessive sulfide residue will cause a secondary pollution.

3.2.2 Leaching-ion exchange treatment[15]

The method is based on decreasing the contents of water-/acid-soluble Cr(Ⅵ) as low as possible. The chromium-containing slag is pulverized to a powder with the size of 0.074 μm, followed by the addition of some water. The digestion agent CO_2 is bubbled into the sludge while stirring. The Cr(Ⅵ) in the solution can be recovered by ion exchange. $BaCl_2$ is added to the residue to fix Cr(Ⅵ) remained in it. By this means, Cr(Ⅵ) can be reclaimed and 96.7% pollution is removed. The equipment is simple and easily maintained. The technology has also advantages of low cost and no secondary pollution. Nevertheless, the content of water-soluble Cr(Ⅵ) in the residue is still higher than 100 mg/kg, which is not agreement with the National Environmental Standard.

Consequently, the methods mentioned above mainly change Cr(Ⅵ) to Cr(Ⅲ) by means of chemical reduction and synthetical treatment. However, chemical treatment still exists some disadvantages of low treatment efficiency, high cost and reappearance of secondary pollution, which limit wide commercial applications. Thus, it is urgent to further develop a feasible technology for detoxification and comprehensive utilization of chromium-containing slag. It is in such a research ground that we put forward to a novel concept for detoxification of the poisonous slag by microorganism.

4 NEW CONCEPT FOR DETOXIFICATION BY MICROORGANISM

Many researchers found that metals at a certain concentration are poisonous to organism. Some microorganisms, however, still have the activities to grow against metal compounds and even metabolize them[16], which shows the character of metal-resistance. Some species of bacteria can even produce a special kind of enzyme, which reduces heavy metals. And they represent certain affinities with some heavy metals. For example, Barton[17] studied the possibility for a bacterium to degrade the toxicity of Se and Pb in solid waste, which shows an excellent action of the bacterium. Certain bacteria also change high toxicity of metals into low toxicity through biotransformation and biological metabolism and make metals detoxification[18, 19]. Other studies[20] show that cyclic-bacillus and acetobacillus can reduce Mn^{4+} involved in manganese oxide into Mn^{2+}. This implies a new progressing direction for treating environmental pollutants containing poisonous heavy metals, such as chromium-containing slag, sediment and so on. The microbial detoxification of chromium-containing slag appears response to the situation in our study.

Up till now, no study on the microbial detoxification of chromium-containing slag has been found. However, there are some reports about the biodegradation on metal electroplating wastewater containing Cr^{6+}, especially the research work made by WU[21]. She used a series of SR combined bacteria that was separated from plating silt to treat metal plating wastewater containing Cr^{6+}. The study received an ideal purpose, and has been applied in commercial practice. On the basis of the mechanism on heavy metals removal by SR combined bacteria, LI[22] designed a new process to treat metal plating wastewater. ZHANG[23] also separated a kind of high efficient reduction bacillus-*Desulfovibrium* from plating silt, which can reduce Cr^{6+} into Cr^{3+} easily being precipitated from water. Some researches were also reported[24~26], for using chromate or bichromate as electron acceptors to reduce Cr^{6+} into Cr^{3+} in the presence of some bacteria, such as *E. coli*, *P. putida*, *S. cerevisiae*, *Pseudomomas dechromatians*, *Aeromonas dechromatica*, *Pseudomonas chromatophila*. Therefore, a few related studies above provide an experimental basis for our research on the microbial detoxification of chromium-containing slag.

Based on the above, a new technological scheme was designed for the microbial detoxification of chromium-bearing slag with the physico-chemical state of the slag being analyzed. The process mainly contains three aspects. Firstly, the acclimation and enrichment of microbial colonies that can detoxify or biotransform Cr^{6+} into Cr^{3+} are carried out. Namely, a sludge or water sample is collected from the site for stacking chromium-bearing slag or plating silt in a plating plant. The initial bacteria specimen is obtained, and then is put into the selected culture medium containing the slag powder for domestication. After a period time of acclimation, those bacteria who can accommodate chromium slag survive. With repeated acclimation and separation, a bacterium with high reducing efficiency and strong life will be got. Secondly, a large scale of inoculum pure culture is done. Thirdly, the process of heap leaching or cell leaching used in bioleaching is adopted to remove the toxicity of the slag. The slag is crushed to powder in certain size, and constitutes a demanded stacking yard, in which many pipes with holes are fixed for pouring or sprinkling the solution including large quantities of high efficient reducing bacteria into the mound from top to bottom. The bacteria and leached metals are collected from the solution at the bottom of the mound. The metals are recovered by a proper process and the bacteria are reutilized.

The technology for the microbial detoxification of chromium-bearing slag shows great advantages compared with other chemical processes. The investment is low and the equipment required is very simple. It can also recover metals. It acts an important role on the poisonous slag treatment and the reutilization of resources. However, the key for receiving a good purpose is to separate and culture the bacteria that can adapt extreme conditions, such as extreme acidity or alkalinity and high metal concentration. Another important aspect is to carry out the bioleaching technology for detoxification of the slag. The technology is full of great potentials for commercial application.

5 CONCLUSION

It is of great significance to carry out the detoxification and synthetical utilization of chromium-containing slag. However, the present chemical methods including pyro-/hydro-based methods still exist some disadvantages of low treatment efficiency, high cost and reappearance of secondary pollution, which limit wide commercial applications. Therefore, a novel concept for detoxification of the slag by microorganism is put forward for promoting high efficient treatment of chromium-containing slag and sustainable development of chromium related industry.

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