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Present State and Prospect on Reutilization of Metal – Bearing Solid Wastes in China

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Abstract: Present states on reutilization of metal-bearing solid wastes in China including metal-containing gangue, red mud, nonferrous metallurgical slag or residue, arsenical slag, steel - iron slag, waste batteries, were described in detail. The wastes pile up at a large quantity, resulting in seriously potential harm to environment. Most of these wastes, however, contain valuable metals, which are regarded as important secondary resources for extracting metals. Waste slag and batteries with a high grade of metals are treated by a hydro-based and / or pyro-based method for extracting valuable metals. While gangue and waste slag with a low grade are as a raw material in architecture field. In the future, a n el technology, such as high-grads magnetization separation technique and biological technique, will be designed to treat these wastes for protecting environment and recycling valuable components. These wastes, furthermore, are synthetically reutilized to produce various architectural materials, including glass and ceramics.
Keywords: metal – bearing solid waste; environmental protection; resource recycling

Introduction

Commercial solid wastes include solid and half-solid substances disposed in the process of industrial production, products processing, fuel combustion, mineral mining and dressing, and environmental harness etc[1]. It was estimated[2] that the total amount of heaped solid wastes has exceeded 6×10^9 t, and various solid wastes increase 1×10^9 t annually. The total amount of heaped metal-bearing solid waste is over 1.5×10^9 t. The waste is predicted to reach 2.5×10^9 t in 2005, since the waste is produced at the rate of 7×10^7 t/a. The commercial solid waste not only occupies a large quantity of land, but also is brought into river and lake. This results in many toxic pollutants into underground water and the environment being polluted seriously. This kind of solid waste, however, contains some valuable metals and deserves synthetical reutilization as a secondary resource.

The resourcization of metal-bearing solid wastes has been widely paid attention and progressed, which is considered as a new economical growth point to the production department. The reuse rate of the waste, however, is still low. Therefore, the paper is aimed at promoting wider use of the solid waste and developing a novel method for the reutilization, through discussing the present status on metal-bearing solid wastes and their reutilization, and putting forward a prospect on the development.

Metal-bearing Gangue and Red Mud

Recovery rate of mineral in the process of mining and dressing is low[3], e.g., the rate is 67% for iron ore, 50 - 60% for nonferrous metals ore. And integrated utilization rate of mineral deposit is less than 25%, the loss amount of metals almost reaches 2×10^9 t. Furthermore, with mineral resource being gradually mined, the outlet of solid wastes including metal-bearing gangue and red mud increases. The total piled-up amount of metal-bearing gangue and red mud is almost 5.835×10^7 t, owns 90% to metal-bearing solid wastes[4]. The reutilization rate of gangue and red mud is only c.a. 3%. This is the main reason that the comprehensive reutilization rate of metal-bearing solid waste is low.

And "Progress of 21 Century in China" determined that comprehensive reutilization rate of solid wastes must reach 50% in 2000, and 65 - 70% in 2010[5]. At present, domestic companies did many studies on reutilization of metal-bearing gangue by recovering valuable metals or producing various architecture materials from the waste, or being used as filling material of ore well. And remarkable achievements have been achieved[6-7]. For instance, Panzhihua Iron Ore Company benefits in reutilizing the gangue over 60% to the total production income. TongLing Copper Company is the earliest factory for developing the gangue in which contains 5.83% sulfur and 28.73% iron. The stacked gangue approximates to 1×10^7 t, the benefits for recycling sulfur and iron from the gangue reaches 2.5×10^7 RMB yuan between 1975- 1988 by a reutilization technology. The heaped gangue in Yunnan Tin Company[8] is over 10^8 t, in which the amount of tin exceeds 2×10^5 t, accompanied with lead, zinc, bithium, copper, iron, arsenic and some other valuable metals. And 1286 t tin and 443 t copper were recovered from the gangue. Average degree of gold, antimony and tungsten in the gangue of Xiangxi Gold Ore are 4.18 g/t, 0.714% and 0.16%, which is deserved to reuse.

Red mud[9] is the disposal residue after extracting alumina from bauxite. There exists 1 - 1.8 t red mud in producing 1 t alumina. At present, average 5×10^7 t of red mud is produced annually in the global. And the domestic amount of red mud reaches 4×10^6 t in 2000[10]. A large quantity of red mud occupies much land, resulting in land alkalization and underground water pollution[11]. Therefore, it is of great importance to reuse red mud. Treatment of red mud is divided into the two aspects, i.e., one is for recovery of valuable metals and extraction of usable components, the other for reutilization of red mud as raw material of architecture industry. Landfill, producing cement and brick, direct reduction for smelting iron, recovery of iron by magnetic dressing, recovery of base etc are current methods for treating red mud.

Smelting Residue or Slag

Primary commercial departments in China for producing solid wastes are for mining, supplying electric power, fuel gas and water, smelting and rolling ferrous metals, manufacturing chemical raw materials and articles, smelting and rolling nonferrous metals, producing food, smoke and juice, producing non-metal mineral, manufacturing mechanical electric and electronic equipments, respectively. The solid waste produced from the above departments owns over 90% of the commercial waste. The solid waste in nonferrous metals industry[6] increases from 6.299×10^7 t in 1990 to 7.721×10^7 t in 1997, with the growth rate being 22.53%. Outlet amount of the waste produced per unit metal decreases from 2.63×10^5 t to 1.33×10^5 t, with reducing 49.4%. Also the comprehensive reutilization rate of the waste increases from 6.08% to 7.96%. The reutilization rate of the solid waste, however, is still very low. The waste piles up at a large scale[12]. It was predicted[13]by Macro-comprehensive Outlet Coefficient method that the amount of the solid waste would be over 8.5×10^7 t in 2005. In addition, steel-smelting slag with 15-20% is produced in producing 1 t steel. And the slag increases at 1.2×10^7 t/a. This causes potential pollution to the environment.

Present outlet amount of the solid waste in smelting department is seen in Table 1[14].

Table 1 Outlet amount of the solid waste in smelting department

Department	Kind and amount of the solid waste
Ferrous Metals Industry	Blast furnace slag: 0.4~1 t / t iron
	Steel slag: 0.2 t / t steel in converter, 0.25 t / t steel in level furnace, 0.15 t / steel in electric furnace
	Iron alloy slag: 2.5~3.5 t / t Si-Fe alloy, 2.8~3.2 t / t Mn-Fe, 1.5~2 t / t Si-Mn, 3~4 t / t V-Fe, 1~1.8 t / t C-Cr-Fe
Nonferrous Metals Industry	Red mud: 0.8~2 t / t alumina
	Smelting copper slag: 0.6~0.8 t / t Cu, lead slag: 0.3~0.4 t / t Pb, Zn-Cu slag: 0.3~0.4 t / t Zn, nickel slag: 0.4 t / t Ni

From Table 1, the outlet amount of the solid waste in smelting department is remarkably large. And an important character of the slag or residue is concerned with rich degree of valuable components, which is reused as the primary secondary resource for recycling metals. It is critical to recycle valuable metals by some novel methods, including hydro- or / and pyro-based metallurgical flowsheets. For example, Jiangxi Guixi Smelter produces almost 1×10^5 t slag from the reverberator annually, from which copper is recovered, gold and silver are concentrated, tellurium is extracted by using flotation – hydrometallurgical technology. Copper and magnesium oxide are recycled from waste magnesium brick in Baiyin Nonferrous Metals Company. Shenyang Smelter recovers gold 15 kg, silver 8 t, copper 26 t annually from the slag in rotation furnace for smelting zinc. And lead 791 t, zinc 3148 t are recovered from the slag in lead blast furnace annually in Shuikoushan Third Smelter. Antimony Mineral Bureau in Hunan obtains antimony 565 t, sodium arsenate 100 t from Sb-As slag annually. Zhuzhou Cemented Carbide Smelter treats tungsten slag for recycling W-Fe alloy, scandium oxide etc by a pyro- and hydro-based flowsheet. Hunan Lianyuan Steel Ltd. Co. used the steel slag as raw materials for producing colorful brick. The developed technology for extracting iron-concentrated powder contains iron 55%, and the slag after separating from the powder is reutilized to manufacture bricks with wide market.

Toxic slags including chromium slag and arsenical slag, especially pollute environments. It is of great importance to harness the pollutants and recover valuable metals from them. Chromium slag is produced over 1×10^5 t annually, the heaped total amount exceeds 2.5×10^6 t. Dissoluble Cr(VI) ion penetrates into underground water, resulting in serious water pollution[15]. Toxic degradation of chromium slag is carried out by pyrometallurgy or hydrometallurgy. The pyrometallurgy is concerned with roasting the slag at a reduction atmosphere. After toxic degradation, the slag is reused as the raw material for producing glass, iron-smelting flux, brick, man-made bone and so on. And hydrometallurgy is by using ferrous sulfate, sulfite and sodium sulfide etc as a reducing agent for changing the valence of Cr(VI) to Cr(III). The detoxified slag, then, is reutilized as architectural materials. Recently, a novel method, bio-degradation, is being developed in our present work.

Arsenic-bearing slag / residue containing valuable metals is the most primary pollution resource in nonferrous metals production of China, which includes smelting waste slag, arsenic-bearing residue after treating waste acid and waste water, arsenic-bearing anodic mud[16-17]. Two methods are applied for treating the above arsenic-bearing slag / residue, i.e., pyrometallurgy including oxidation roasting, reduction roasting and vacuum roasting, hydro-based flowsheet on acid leaching or base leaching. Furthermore, some novel technologies for treating the waste appear, e.g., synthetical recovery of antimony, arsenic, base and other valuable components from arsenic-bearing slag or residue by pressure oxidation leaching method.

Waste Battery

Increase in battery usage means the increase in waste battery. Waste batteries in China are originally from city municipal, commercial departments, manufacture factories and metals recycling companies etc. Chinese government pays high attention to recycling waste batteries, and "21 Century Green Life Proceedings" was organized in State Environmental Protection Administration of China[19]. It is the first that classification and recycling of waste batteries from rubbishes were carried out in the four cities including Beijing, Shanghai, Guangzhou and Nanjing in 2000, promoting a wide action in all over China. Many efficient methods have been applied and management system of waste batteries has been gradually formed.

China lies in the first for producing battery, which occupies half of the total amount in the world. It is stated that the amounts of dry batteries in China reaches 1.25×10^{10} pieces in 2000. Consumption amounts of batteries approximate to 1×10^{10} pieces annually, most of which are deserted. The waste is a harmful and hazardrous pollutant, which contains many metals, such as Hg, Cd, Zn, Mn, Cu, Ag, Li, Ni, Pb etc, without variation of the prosperities and states in using the battery. On the other hand, vast amounts of nonferrous metals, however, are valuable resources. The degrees are more than that of ore. It is estimated that annual consumption amounts of zinc used in battery are 2.4×10^5 t (almost 1/13 in domestic total production amounts of zinc), manganese oxide 2.8×10^5 t, zinc chloride 3.3×10^4 t. In addition, it is reported that consumption amounts of Pb in storage cell owned 68% to the total consumption amounts in 1997, and will reach 85.48% in 2010, which means that the amount approximates to 3.847×10^5 t[18]. Waste lead-acid storage cell is discharged to c.a. 3×10^5 t annually, the recovery rate of the waste battery and the recovery rate of lead, however, are merely less than 90% and 80% respectively. Therefore, it is of great significance to recycle the valuable components from the waste and carry out harmlessness and minimization of the waste.

Waste batteries can be classified into six categories, i.e., alkaline zinc-carbon or manganese battery, mercury oxide battery, silver oxide battery, nickel-cadmium battery, lithium and lithium ion battery, lead storage battery, on which different methods are applied for treating the waste.

Generally, waste batteries are recovered by hydrometallurgy or pyrometallurgy. The former is on the basis of the hydro-based principle that valuable components in waste batteries are dissoluble in acid. After purification, metals including Zn, Pb, Ni, Cd, Mn and / or their compounds are produced by electrolysis or precipitation. The later is concerned with oxidation of metals or compounds, reduction, decomposition, volatilization and condensation, which includes metallurgy at room pressure and vacuum metallurgy[20]. Disadvantages exist in hydro-based methods and pyrometallurgy at room pressure. And vacuum metallurgy is a prospectus direction for recycling waste batteries because of short flowsheet, low energy consumption, no pollution to environments, high reutilization rates of valuable components.

Prospects

Comprehensive reutilization of metal-bearing solid wastes has been progressed, however, the reutilization rate is still low, and the pollution to environment is serious. It is of great urgent to develop a novel technology for harness and reuse of metal-bearing solid wastes, e.g., biological technique, high-grads magnetization separation technique so as to progress industrization of the comprehensive reutilization of the waste.

Biological technique

The degrees of valuable components containing in tailings, red mud and various slags, sludge, in general, are low. The disadvantages of hydro-based method include excessive consumption of chemical reagents, high costs, and attendence of vast amounts of secondary waste residues. Pyro-based method, however, also exist some shortages, including high invest for equipments, high consumption of energy, serious secondary pollution of waste gases and dusts. Thus, on the basis of the characteristics of metal-bearing solid wastes, which include low degree of metals, strong toxicity, it is a prospective method that the metal-bearing solid waste is comprehensively harnessed and reutilized by selecting a high efficient bacterium inoculum and applying a cell leaching or heap leaching technology. This method needs low cost, and does not exist secondary pollution. With regarding this, a novel bio-hydrometallurgical technology is being developed for treating a poisonous chromium slag and arsenical slag or residue in our present work.

High-grads Magnetization Separation Technique

Complexity of constituents in solid wastes results in different properties of the constituents, such as magnetic property, particle size, density, electric property, chemical constitutes. It is by using the difference of magnetic property among constitutes that valuable components are separated from each other and from harmful components by high-grads magnetization separation technique[21]. It is of great benefit that the technique resolves some difficult problems without being resolved past, which is full of wide application prospects in the field of comprehensive utilization of metal - bearing solid wastes.

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