Utilizing steel slag in environmental application - An overview

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Abstract. Steel slags are generated as waste material or byproduct every day from steel making industries.The potential environmental issues which are related with the slag dump or reprocessing for metal recovery are generally being focused in the research. However the chemistry and mineralogy of slag depends on metallurgical process which is able to determine whether the steel slag can be the reusable products or not. Nowadays, steel slag are well characterized by using several methods, such as X-ray Diffraction, ICP-OES, leaching test and many more. About the industrial application, it is mainly reused as aggregate for road construction, as armour stones for hydraulic engineering constructions and as fertilizers for agricultural purposes. To ensure the quality of steel slag for the end usage, several test methods are developed for evaluating the technical properties of steel slag, especially volume stability and environmental behaviour. In order to determine its environmental behaviour, leaching tests have been developed. The focus of this paper however is on those applications that directly affect environmental issues including remediation, and mitigation of activities that negatively impact the environment.

1. Introduction

Various types of slags are generated as waste material or byproduct in metallurgical process. Based on its origins and characteristics, the main slags can be categorised into three major types, such as ferrous slag, non ferrous slag and incineration slag. In terms on its mineral composition, slag usually contains quantities of valuable metals. It's generally possible to recover some values by physical or chemical mineral processing techniques, such as crushing, grinding, classification, hydrocyclone, magnetic seperation, flotation, leaching or roasting [1]. Another feature of steel slag is that the releasing on notable amount of heavy metals which can cause the environmental problem. Furthermore, the steel slag dumping is the most conventional disposal method. The increasing of steel slag dump is not only causing the scarcity of the landfill, but also potentially have an impact to the environment, especially water pollution. Therefore, the metals revovery and utilization of steel slags

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are highly desirable. Characterization of the environmental aspects of steel slag helps to evaluate its potential to release contaminants and its suitability as a potential resource [2].

2. Properties of steel slag

2.1 Physical properties
Steel slag aggregates are highly angular in shape and have rough surface texture. They have high bulk specific gravity and moderate water absorption (less than 3%). The grindability index of steel slag is 0.7, in contrast with the value of 0.96 and 1.0 for blast furnace slag and standard sand respectively [3].

2.2 Chemical properties
The chemical composition of slag is usually expressed in terms of simple oxides calculated from elemental analysis determined by X-Ray Fluorescence (XRF). Virtually all steel slags fall within these chemical ranges but not all steel slags are suitable as aggregates. Of more importance is the mineralogical form of the slag, which is highly dependent on the rate of slag cooling in the steel-making process.

2.3 Mechanical and thermal properties
Processed steel slag has favorable mechanical properties for aggregate use, including good abrasion resistance, good soundness characteristics, and high bearing strength. Due to their high heat capacity, steel slag aggregates have been observed to retain heat considerably longer than conventional natural aggregates. The heat retention characteristics of steel slag can be advantageous in its resistance toward high temperature effects.

3. Steel slag characterization

3.1 Scanned Electron Microscopy (SEM)
SEM is a device that utilizes focused beam of high energy electrons to analyze solid material by obtaining topographical, morphological and compositional information of the tested sample. A scanning electron microscope (model S -3400N, HITACHI, Japan) was used to obtain external morphology, crystalline structure and orientation of materials making up the sample at an accelerating voltage of 20.0 kV, beam current of 50 mA and working distance of 9.0 mm – 10.0 mm using backscattered electrons (BSE) objective with aperture of 3. Two images were captured at a low magnification (300×) and high magnification (1000×) respectively. The micrographic appearance of the unreacted EAFS shows distinct mineral phases, presented in Figure 2. The light areas contain a higher proportion of Fe, Mg, Mn and Al while the dark areas contain a higher proportion of CA and Si [4]. From Figure 3, it can be seen that the light areas are larger than the dark areas. This indicates a hig her composition of Fe, Mg, Mn and Al compared to the composition of Ca and Si
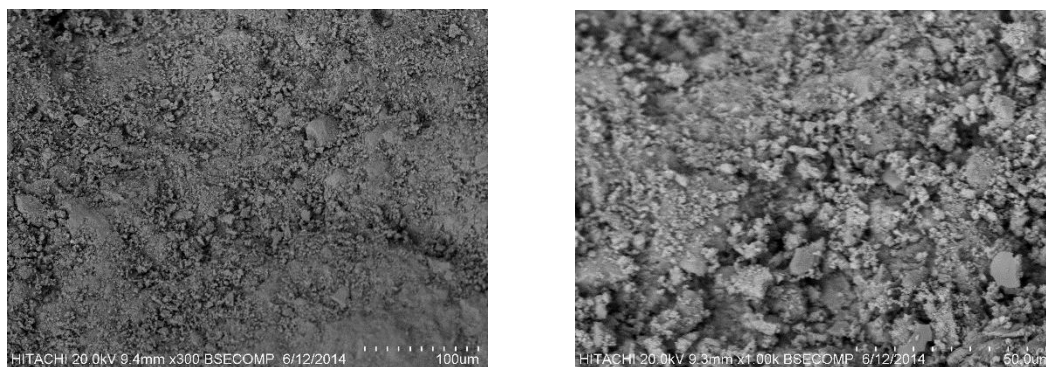
Figure 1. SEM micrograph of unreacted EAFS at magnification of (a) 300x and (b) 1000x

3.2 X-Ray Diffraction (XRD)
X-Ray diffractometer (model XRD-600, Shimadzu, Japan) was used for phase identification of unreacted EAFS with Cu Kα radiation at 40 kV and 40 mA and scanned between 2θ = 20°–80° and scanning speed of 0.1°/min. The X-Ray diffraction pattern observation was generated by using powder diffraction method. The XRD pattern was then analyzed using X'Pert High Score Plus software to obtain the mineralogical and chemical composition of the sample slag. Each crystalline solid has its unique characteristic XRD pattern which may be used for its identification. X'Pert High Score Plus software has the database of these XRD patterns so that they could be used to match with the peaks appear in the XRD pattern of unreacted EAFS. Once all the peaks were identified for the chemicals present in the sample slag, the intensity under the peaks was automatically used by the software to determine their composition.

The XRD analysis of unreacted EAFS is shown in Figure 2. The diffraction pattern is heterogeneous, consisting of a mixture of crystalline phases. The analysis identifies calcium oxide (CaO), silicon oxide (SiO_2), hematite (Fe_2O_3), manganese (III) oxide (Mn_2O_3), magnesium oxide (MgO), aluminium oxide (Al_2O_3), phosphorus oxide (P_2O_5), metallic iron (Fe), srebrodolskite ($Ca_2Fe_2O_5$), dicalcium silicate (Ca_2SiO_4) and pyroxene ($CaAl_2SiO_6$).
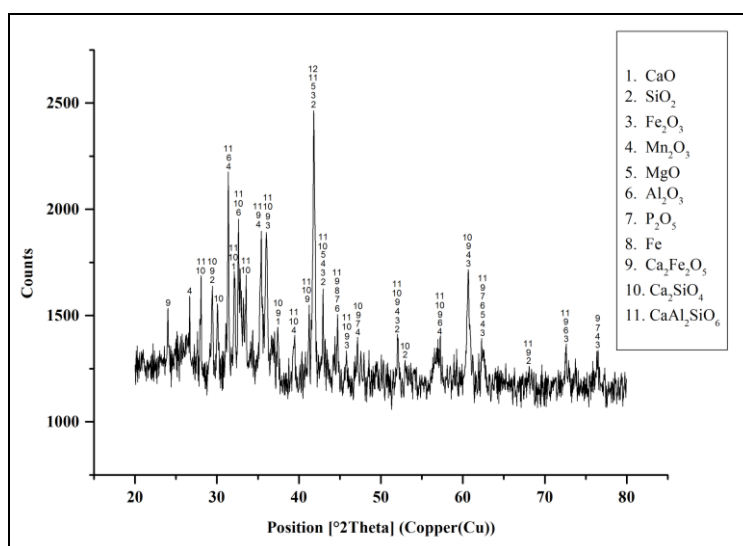

Figure 2. XRD pattern of unreacted EAFS

3.3 Inductively Coupled Plasma Optical Emission Spectrometry
Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an elemental analytical technique used to determine the composition of a wide variety of materials in liquid form, with excellent sensitivity. In this study, leachates from the experiments manipulating the initial concentration of HCl and EAFS size were diluted and sent for elemental analysis using Inductively Coupled Plasma Optical Emission Spectrometer (model Optima 7300DV, Perkin-Elmer, USA) to determine the concentration of the elements Fe and Ca. Calibration curves for Fe and Ca of known concentration 0 ppm – 9 ppm and 0 ppm – 90 ppm, respectively was prepared for the determination of concentration of Fe and Ca in the samples.

4. Applications of steel slag
According to the Malaysia Environmental Quality (Scheduled Waste) Regulation (2005), Steel slag is classified as non-hazardous waste which can be disposed off to appropriate landfills. The disposal of steel slag requires large landfill area which is rather unfavourable in economical terms. Therefore, several research and development have been conducted to establish the potential use of slag in different applications. However, it might have the risk that different components of slag might elute, especially on the heavy metal. Therefore, it is necessary to examine this metallurgical waste material in appropriate ways. Typical applications of steel slags are sealing aggregate (skid resistant), asphalt aggregate, base, sub-base, construction fills, subsoil drains, grit blasting and waste water treatment. The various applications for steel slag in 2010 (22.3 million tonnes) is illustrated in Figure 3
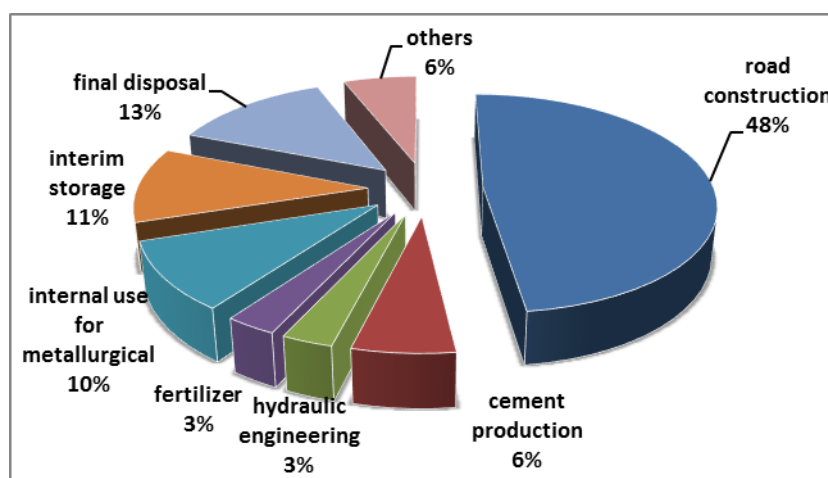

Figure 3. Statistical data of various applications of steel slag (2010) [5]

4.1. Cement production
In cement and concrete industries, slag can be used either as an aggregate or binder in stabilized base courses. In order to conserve natural resources and reduce environmental impact, slags can be used as an aggregate. To diminish the need for cement which is expensive in cost, slag is replaced and used as a binder. Because of these advantages, many researchers have examined adding slag content to cement and concrete [6]. Addition of slag to cement presents some important technical advantages over ordinary Portland cements. These benefits can be enumerated as development of mechanical strengths, low solubility of the hydrates and porosity, lower heat of hydration, excellent durability and stronger aggregate–matrix interface. However, there are some disadvantages such as high shrinkage, formation

of micro-cracks and rapid setting. Therefore, the combination of various type of slags (activated, chemical and physical modified) to cement are investigated. For instance, it can boost the hydration ability of slag cement concretes, improving the mechanical performance of cement, enhancing the strengths of cement, autogenous deformation on the cracking, microstructure and durability, resistance.

4.2 Road construction
Industrial by-products such as steel slag can be utilized instead of natural aggregates in order to prevent depletion of resources. Million tons of sand, till and crushed rocks were extracted from mines due to roads construction. It is well known that technical, economical and many environmental benefits are obtained when steel slag has been considered as alternative construction materials [7]. Due to prominent properties of steel slag, it is an ideal aggregate for asphalt surface course materials and road surface treatments. It has been proven that the use of steel slag in road construction mixtures has more advantage compared to conventional asphalt. The investigations of the asphalt mix and road surface have shown very good results in terms of stability, stiffness and durability. The slag asphalt, as expected, provided good friction values, noise reduction levels, enhances resistance to cracking at low temperatures with excellent performance in roughness and good resistance against water permeability[8].
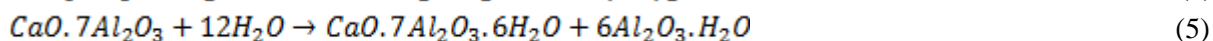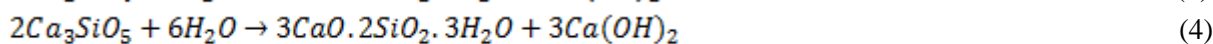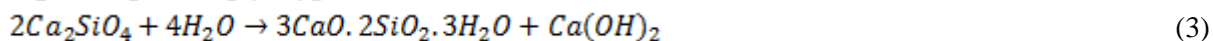
4.3 Phosphurus removal
Phosphorus (P) from agricultural wastewater is one of the major pollutants in natural water that cause the algae growth and eutrophication of lakes. Therefore, Phosphorus is one of the major nutrients that is need to be removed from domestic wastewater before being discharged into water bodies. The application of an appropriate technology to remove the maximum capacity of nutrient is imperative. In order to remove phosphorus from wastewater, various methods or approaches have been attempted, including biological, chemical process (precipitation, metal salt addition) and physical (electro-dialysis, reverse osmosis). Among all the methods, the chemical precipitation is expensive and increasing sludge volume by up to 40%. The biological phosphorus removal needs a lot more volume or space (anaerobic unit) than the other processes. Various research on the potential use of industrial by-products to remove P from wastewater was studied in the late 1980s.

The P removal is along with the development of constructed wetlands (CW). This method is a low cost technology for pollutions treatment, which slag performs an important role in absorbing impurities especially phosphorus. By comparing most of industrial by products, steel slag is a low-cost and abundant material, which its combination with small secondary treatment systems (such as constructed wetlands) is preferred in compared to the others methods [9,10]. The slag contains various metal oxides such as iron oxides and alumina that may be effective in P reduction from domestic, agricultural effluents and municipal [11]. Steel Slag is a light weight porous medium with numerous sites for sorption. Steel slags have different physic-chemical property due to various feedstock ores, fluxes and manufacturing process. These differences caused a board range of P sorption capacity by using slag, ranging from 76.4 to 8390 mg/kg. Many experiments have been carried out in laboratory to evaluate the sorption capacity of slag. These studies have found slag to be a promising substrate for P-removal [12].

4.4 Water and wasteweater treatment
As slag has good sportive characteristics and is low cost, it is widely used in wastewater and water treatment, and may be the alternative of using granular activated carbon. Various research such as adsorptions of dye, heavy metals and organics were carried out by using steel slag. However, the uptake capacity of slag is dependent on the pH solution. The hydration of slag composition in the

aqueous solutions provides a high pH. The possible hydration reactions can be occurred with different compositions of slag as followings:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1)$$
$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (2)$$
$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 \qquad (3)$$
$$2Ca_3SiO_5 + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \qquad (4)$$
$$CaO.7Al_2O_3 + 12H_2O \rightarrow CaO.7Al_2O_3.6H_2O + 6Al_2O_3.H_2O \qquad (5)$$

With the high pH condition, the slag surface is negatively charged and adsorption metal ions especially cations are preferred. However, heavy metal absorption by using slags can be conducted with a condition of either high temperature or low pH under certain conditions. Yamashita et al. investigated the possible mechanisms of removing dissolved heavy metals from aqueous waste liquids via the converter furnace slag [13]. They suggested that the removal can be attributed to one or more of following effects: adsorption, co-precipitation, hydroxide precipitation as hydroxide, sulphide and ion exchange.

Wastewater from the steel mill contains a high concentration of heavy metals due to the accumulation of filtered particles from the filtration process of wastewater. A direct release of the backwash water into the environment may cause serious effects to both land and aquatic lives. Based on the toxilogical studies, metals are toxic and non-biodegradable and may continue to exist in these water bodies. Furthermore, the heavy metals also have the tendency to accumulate in the food chain. Hence, a strict environmental regulation has been established in an effort to mitigate the heavy metals contamination of the discharge of industrial effluent. Absorption of lead ions by two different types steel slag was carried out in column-type contact process [14]

5. Steel slag leaching

Extraction of metal values from mineral wastes are major steps towards conservation and judicious utilization of our mineral resources which are depleting very fast. Electric Arc Furnace (EAF) Steel Slag is an abundant byproduct in steel industry. The EAF slag contains considerable amount Fe and Ca oxides. By recovering the metal values, these slags would become value added products instead of being considered as pollutants. The EAF slags can be converted to metal chlorides, namely ferric chlorides and calcium chlorides. Ferric chloride is a flocculant used in the wastewater and water industry. Calcium chloride finds application as brine for refrigeration and as adsorbent for fluoride removal.

Extraction of metal values from the EAF slag would convert waste to wealth. The chloride process route has shown a lot of promise. Metal chlorides can be produced from EAF slag by the applications of various chlorinating agents like gaseous chlorine and hydrochloric acid. Ferric Chloride can be used as a flocculant in sewage treatment and drinking water production, and as an etchant for copper-based metals in electronic industries. Calcium chloride applications include brine for refrigeration, dessication and also to remove fluoride in water and wastewater treatment. This EAF slag is free and abundant and is therefore an ideal raw material or low cost production of metal chlorides.

Although it seems reasonable the use of chlorination method for the recovery of refractory metals from EAF slags as their chlorides and oxy-chlorides mixtures, it is the fundamental importance a study that defines the further chemical processing of this mixture. For such, it should be taken into consideration the nature of the desired final products, ferric chloride and calcium chloride as well as their possible uses.

According to the study done by Brocchi and Moura (2008), the conversion of ferric oxide and calcium oxide are relatively much higher than other metal oxides present at a lower operating

temperature compared to the reaction with gaseous chlorine [15]. Since the chlorination of ferric oxide and calcium oxide are the only main concern, batch leaching of EAF slag with hydrochloric acid is selected as the chlorination method. The operating parameters are chosen and manipulated by referring to the literature done as well.

6. Conclusion

In this review, widespread usage of slags as a by-product of steel making industries in various applications have been discussed. In terms of steel slag characterization, XRD, SEM and ICP-OES are being used to determine the mineral compostion of steel slag. Based on the literature studies, it is pretty obvious that slags can be the promising replacements for conventional way of application of adsorbent and binder in various fields such as adsorption, construction, road and waste water treatment. The ease of use, low cost, and sources availability are among the few advantages on reusing and utizing the steel slag. On the other hand, the methods of steel slag leaching with hydrochloric acid are developed in order to recover the valuable metals in steel slag. Therefore, by implementing all the remediation, and mitigation of activities as per mentioned above, our environment can be protected.

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