

Absorption of Lead Ions by Various Types of Steel Slag

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ABSTRACT: *Steel slags are the by products of steel industries, which forms during reduction process of iron melting. The chemical composition of it changes depending to the melting procedure. Its mineralogical composition also varies based on the cooling procedure. Two different types of steel slag were used as absorbing bed for various concentrations of Pb^{2+} ions in the form of lead chloride, and the concentrations of lead ions were measured in the effluent by atomic absorption spectroscopy. When Electric Arc Furnace slag (EAFS) which is a basic crystalline slag was used in the presence of various concentrations of Pb^{2+} , ranging from 2mg/lit up to 10 mg/lit. The concentration of lead ions dramatically decreased in the first thirty 30 minute and the remaining ions were absorbed up to 48 hours that the reaction was continuing but with slower rate. Almost the same thing happened when granulated blast furnace slag (GBFS) which is also a basic slag but in the amorphous mineralogical form, was used as the absorbing bed. The extent of ion removal from the solution was much lower compared to EAFS. Based on the results of this study, both types of slags can be used as industrial filters for reduction of lead ions from industrial waste waters.*

KEY WORDS: *Granulated blast furnace slag, Electric arc furnace slag, Absorption of lead, Atomic absorption spectroscopy.*

INTRODUCTION

Slags are the final wastes from the steel industry. Although they are, in fact, classified as wastes, they have been widely reused for various purposes for a long time. In 1993 the European Waste Catalogue did not include any slag and the council of the OECD (Organization for Economic Cooperation and Development) decided in 1995 to exclude all slag materials, which meet the related standards, from the list of wastes [1]. Thus slag is currently considered as a product, not as a waste. Slag has been used as a fill material in road construction, a phosphatic fertilizer, or a method for water and

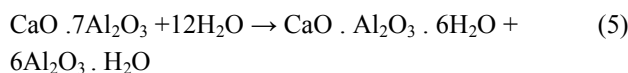
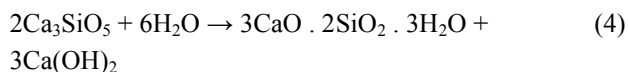
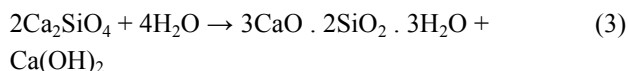
wastewater purifications [1-3]. For its sorptive characteristics, slag has been used in water and wastewater treatments as a low cost adsorbent replacing granular activated carbon (GAC). Adsorptions of dye, nickel, phosphorus, and lead are the examples [4-6]. However, the adsorption capacity of slag is pH dependent and the hydration of slag composition should provide a high pH in the aqueous solutions. Major hydration reactions may occur with calcium oxide, magnesium oxide, calcium silicates, and calcium aluminate as followings [7]:

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1021-9986/08/3/69

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Under the high pH condition, the slag surface is negatively charged and adsorbs cations, such as sodium and metal ions [3-6]. Dissolution of slag and adsorbed metal ions occurs with a condition of either low pH or high temperature [6]. With the various pH environments the properties of slag may change and release of toxic elements may occur through the leaching process [7].

Lead has a specific toxic and cumulative effect and its discharge into environment represents serious threat to many life forms. Industrial waters from battery manufacturing, metallurgy, metal finishing, chemical industry, etc., belong to the main Pb pollution sources. Lead in these waters should be reduced to levels in correspondence to the rules of regulatory agencies. The usual method for removal of lead is chemical precipitation [8,9]. Sorption processes including ion exchange and adsorption are an alternative with great potential to treat water and wastewaters containing heavy metals [10,11].

The main disadvantage of the sorption method consists in the high price of the adsorbents, which increases the price of the wastewater treatment. Some of these materials combine good adsorption capacities and buffering effect, which assure almost complete removal of heavy metal ions without preliminary correction of the initial pH being necessary. Blast furnace slag from ferrous metallurgy is a complex mixture of alkali-earth silicates and aluminosilicates formed at high temperatures in the blast furnace. Earlier research [12,13], has shown that the blast furnace slag is a good adsorbent towards copper, zinc, nickel and lead ions. Granulated blast furnace slag also has a suitable particle size and good filtering properties. The alkali or buffering effect of blast furnace slag in aqueous solutions determines some peculiarities of the process of elimination of heavy metal ions and is one of the reasons for which the mechanism of

the process cannot be defined explicitly. It is known that heavy metal adsorption is effective in an alkaline region. However, when the medium pH is controlled by the adsorbent (as in the cases of various alkali and alkali earth silicates), the mechanism of heavy metals removal is difficult to determine. According to *Dushina* and *Aleskovaski* [14], the ion exchange is a first step of metal ion detention on the surface of various calcium silicate materials, including slag. Depending on the nature of the material and the conditions of the experiment, the process may continue with further interactions between the metal ions and the solid matrix. The formation of sparingly soluble compounds of the type of metal silicates (surface precipitation) is possible.

Yamashita et al. [15] have reported that the mechanism of adsorbing and fixing heavy metals of the converter furnace slag can be attributed to one or more of following effects: adsorption, co-precipitation, hydroxide precipitation as hydroxide, sulphide and ion exchange.

The aim of this study was to establish the possibility of using granular blast furnace slag (GBFS) and/or electric arc furnace slag (EAFS) columns for treating industrial waste waters containing heavy metal ions. Lead was chosen as a representative of the heavy metals as one of the most widespread pollutants and, besides, has already been investigated in batch-type contact process. The main task of the study was to determine the effectiveness of the lead removal process in GBFS and EAFS column depending on metal ion concentration, particle size, bed contact time, etc.

MATERIALS AND METHODS

The GBFS used was a commercial by-product of the Esfahan steel company it was water jet cooled (granulated), hence in the amorphous state, while Electric Arc Furnace slag was produced by Mobarekeh steel company, it was an air cooled slag in the crystalline form. Their chemical compositions as received from the plants labs are shown table 1. This is the average values of their slag production from two weeks.

The mineralogy of slags was examined by a Philips Pw-1730 diffractometer using monochromatic Cu K α radiation. The X-ray spectra of the slags are shown in Figs. 1 and 2. The former is X-ray diffraction pattern of EAFS. According to these spectra, the slag is completely crystalline composed of crystals of wustite, magnetite and

Table 1: Chemical composition of different steel slags.

Chemical composition wt %	GBFS	EAFS
CaO	36.00	41.50
MgO	12.00	9.00
SiO ₂	36.00	15.00
FeO	1.00	26.00
Al ₂ O ₃	10.00	6.50
MnO	1.00	2.00
TiO ₂	3.00	----

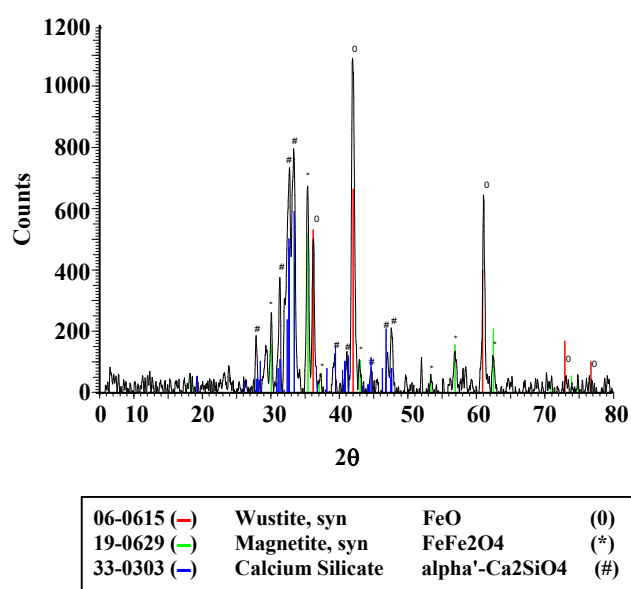


Fig. 1: X-ray diffraction pattern of EAFS.

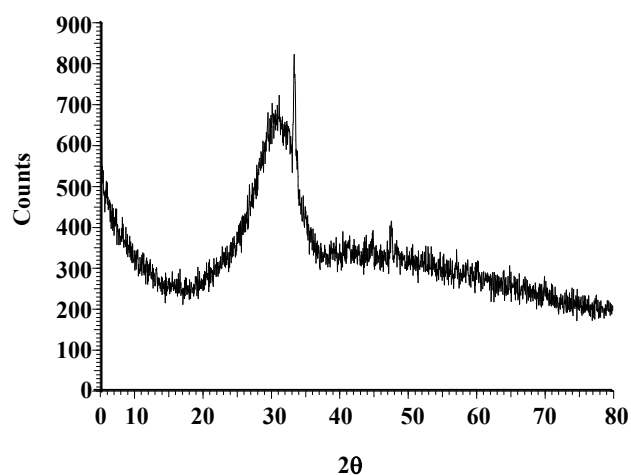


Fig. 2: X-ray diffraction pattern of GBFS.

calciumsilicate, whereas the latter is the pattern of GBFS, it showed no peak, which indicated an amorphous structure. Both slags were fractionated, rinsed with distilled water to remove fines, dried at 105 °C and stored in a bank. All working solutions were prepared using reagent grade metal chloride salts and distilled water. The ionic concentration was ranged between 2 and 10 mg/lit (ppm) based on the concentration of Pb. The pH measurements were made using a pH meter (TM-6). The concentrations of metals were conducted by atomic absorption spectrometer Perkin Elmer model AAnalyst 300 (AAS). Column experiments were conducted in a glass column (5 cm ID) packed with GBFS or EAFS. Two different particle sizes of both slags were used (0.25-0.50 and 0.50-2.5 mm). The apparent density was measured as 1.27 g /cm³ and 1.29 g /cm³ respectively. The slag bed height was 31 cm. The Pb-containing influents were passed downward through the column with linear flow rates of 4.5 cm/min. The effluent samples from both were collected regularly and analyzed without previous filtration. Every time part of the effluent was collected, it was replaced by fresh lead solution with appropriate concentration on the top of the column to fill up with the mark level.

The stock solutions were prepared by using of analytical grade lead salt manufactured by Merck Company. Four different standard solution concentrations were prepared in order to get a linear standard curve introduced by manufacturer of the AAS instrument.

All the following experiments were carried out with untreated GBFS and EAFS due to its higher removal efficiency.

RESULTS AND DISCUSSION

Measurement of pH of slag in pure water

1- In order to examine the alkaline effect of the GBFS and EAFS in different columns, a separate set of column experiments were carried out with an influent without lead ions. Relatively high and constant effluent pH values (8.9-9.2) were observed for GBFS and (9.0-9.4) for EAFS respectively after which the effluent pH dropped sharply.

It is due to hydrolysis reaction the slag can slowly release hydroxyl ions in the aqueous phase, *Dimitrova, S.* [16]. Since the influent passing through the column has an enhanced H⁺ content, the hydrolysis is probably

accompanied by an exchange reaction between the calcium ions of the slag and the hydrogen ions in the influent. The results from interruption experiment also suggest that these processes can occur both on the slag surface and in its bulk. The pH and Ca curves tend to decrease during all runs, despite the experimental conditions, *Dimitrova, S.* [17].

2- The effect of GBFS on various concentrations of lead solutions; Various concentrations of lead salt were used as the influent on the column filled with two different types of steel slags. At the required time intervals, 30 ml of effluent was collected in order to investigate the effect of time on the absorption of lead by slag. The concentration recorded each time was based on the amounts of lead presented in 30 ml of effluent. The beginning concentration was 2 mg/l, based on the concentration of lead. The results are graphically shown in Fig. 3. According to this results, when concentration of lead is low, much of it absorbs at first 30 minutes by steel slag, but after about 2 hours, a few milligrams of lead starts to leach out into the solution and absorbs by lead simultaneously but, the rate of absorption is lower hence, the concentration of lead ion increases at longer times steadily.

The second sets of experiments were done with the higher concentration of lead chloride which was 5 mg/lit according to the concentration of lead. The results of these sets of experiments are also graphically shown in Fig. 4. Based on these results, much of the lead was absorbed after half an hour, but its concentration in solution started to increase by leaching of lead into the solution from slag. Leaching of lead into the solution was continued up to 48 hours by a smooth constant rate, while the experiment was running.

When the concentration of lead was increased up to 10 mg/lit in the influent water, much of the lead ion was absorbed at the beginning of reaction, the same as lower concentrations. The results are shown in Fig. 5. Based on this figure, the amount of lead in the effluent water dropped to dramatically after 30 minutes of absorption by steel slag, but lead started to leach back into the solution. The leaching continued up to 8 hours, but at longer time intervals, like 24 hours, it absorbed by slag and its concentration dramatically reduced with the same trend up to 48 hours. It seem from the whole sets of

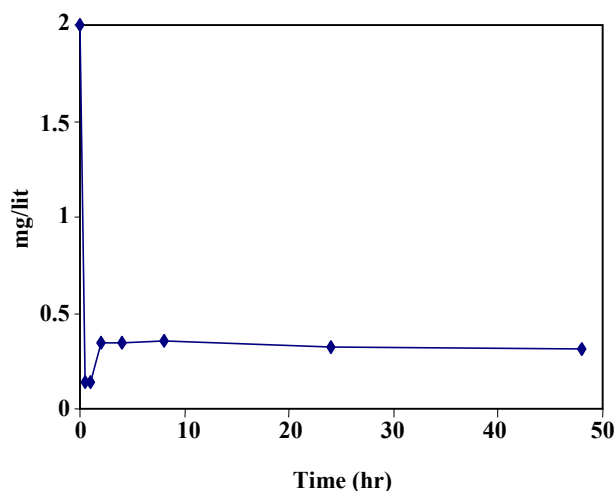


Fig. 3: The effect of GBFS on 2 mg/lit solution of Pb²⁺ ions.

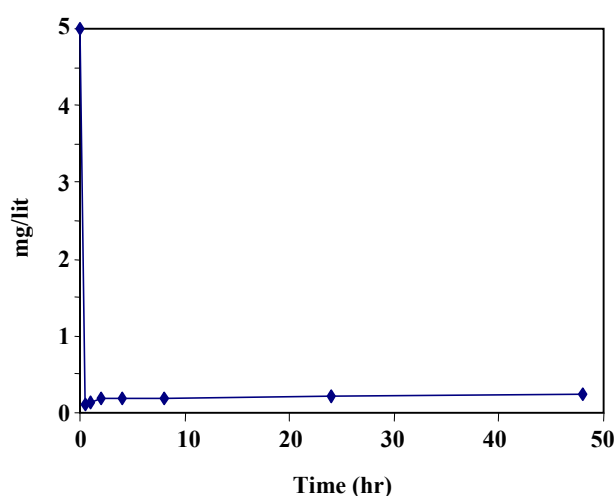


Fig. 4: The effect of GBFS on 5 mg/lit solution of Pb²⁺ ions.

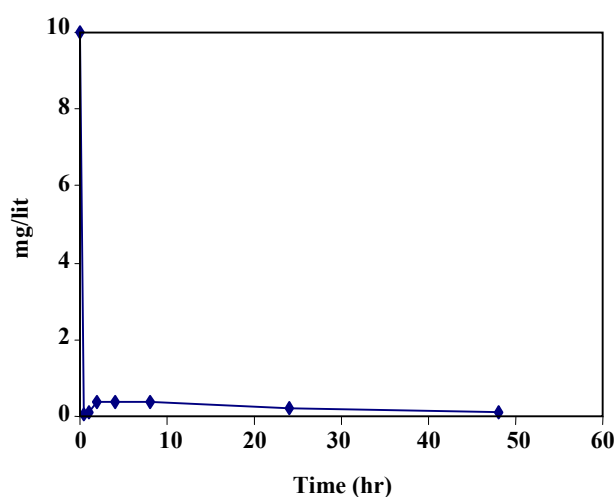


Fig. 5: The effect of GBFS on 10 mg/lit solution of Pb²⁺ ions.

experiments that lead ions absorb by steel slag dramatically and the amounts of absorbing ion depends on the lead ion concentration of influent.

3- The effect of EAFS on various concentrations of lead solutions; The same sets of experiments were done on absorption of lead ion by EAFS as previously explained about GBFS. In this case, the story was a bit different than when GBFS was the absorbing bed. When the 2 milligram per liter of lead ion passed over the absorbing bed, about fifty percent of it was absorbed at the first thirty minutes of reaction, the absorption continued but with lower rate. As it can be realized from the Fig. 6 which is drawn based on the results of these experiments, at later times, about 0.2 milligrams of lead was absorbed every one hour after first half an hour of the beginning of reaction. After 24 hours the concentration of lead was about 0.01 milligram and the whole lead ions was absorbed after forty eight hours of reaction.

When higher concentration of lead such as 5 mg/lit passed over EAFS, the concentration of lead dramatically dropped into 0.05 milligram per liter after thirty minutes, this stayed constant after one hour of reaction. Lead ions were absorbed by EAFS in a smooth rate at longer times and its concentration was measured to be about 0.1 mg/lit after forty eight hours of reaction. The results of this sets of experiments are graphically shown in Fig. 7.

At higher concentrations of lead in the influent water like 10 mg/lit, much of the lead (about 98 %) was absorbed by slag at the first 30 minutes. At longer times, lead leached into the water and its concentration increase to about 0.04 mg/lit after 4 hours of reaction, while at longer time, slag become activated and absorbed the leached lead. The lead ions were absorbed after 8 hours and its concentration was constant up to 48 hours that the experiment was running. These results are shown in Fig. 8.

This behavior of EAFS is possibly due to its crystalline mineralogical composition which is shown by X-ray diffraction pattern in Fig. 1. The total crystalline nature of this slag is due to the slow cooling process of it from the melt.

4- Metal removal mechanism; The column results obtained are very important and are directly associated with the mechanism of the process taking place in the column. On one hand, the high pH values and the relatively high lead concentration result in the formation of hydroxyl lead forms and their coagulation/precipitation

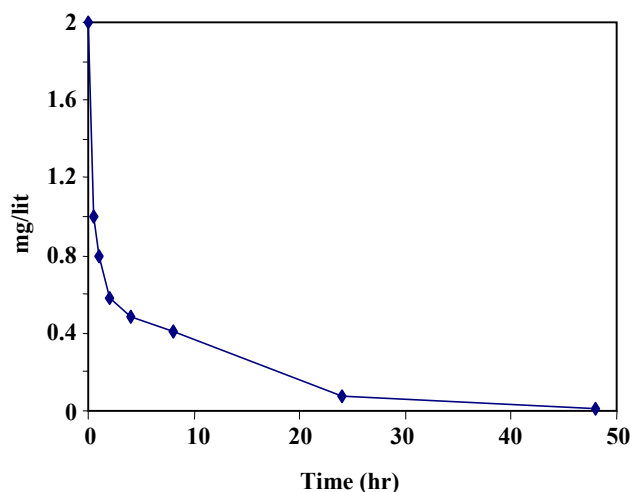


Fig. 6: The effect of EAFS on 2 mg/lit solution of lead ions.

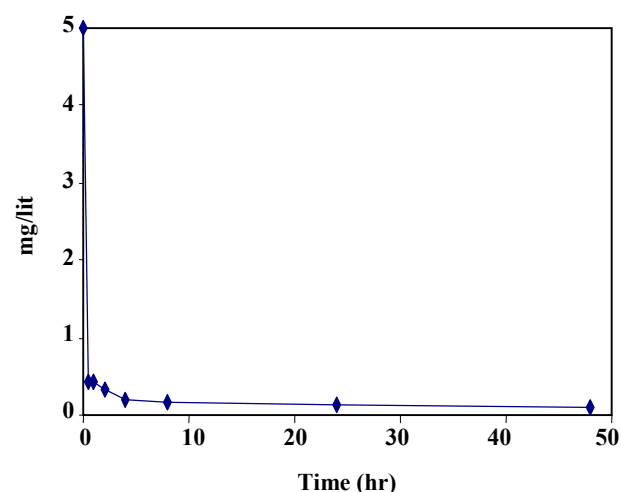


Fig. 7: The effect of EAFS on 5 mg/lit solution of lead ions.

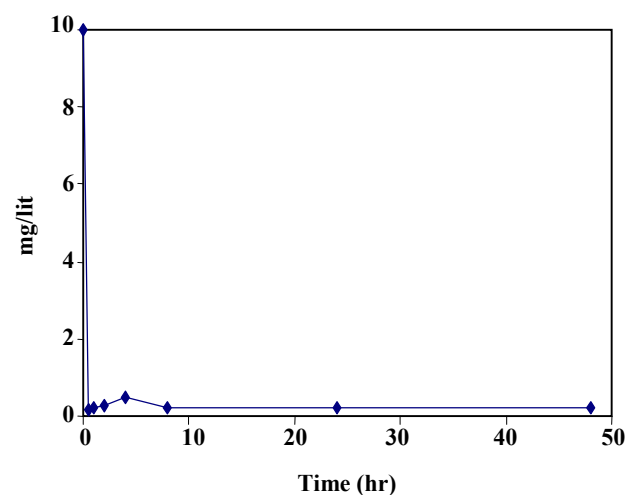


Fig. 8: The effect of EAFS on 10 mg/lit solution of Pb^{2+} ions.

on the slag surface and in the space between the particles are prevailing. On the other, since the precipitation kinetics is slower than adsorption or ion exchange kinetics, the removal of lead cannot result solely from precipitation as hydroxide. Having in mind the slag nature, it is difficult to determine which surface species (AlOH, AlO⁻, SiOH, SiO⁻) is responsible for lead removal. Since the slag has more Si than Al, so the silica surface sites should predominate. They are occupied by calcium and when GBFS placed in aqueous solution both hydrolysis and ion exchange processes begin. Under experimental conditions used in this study, the surface calcium is changed by the hydrogen ions and lead ions.

In the case of EAFS, it is possibly suggested that lead may have gathered in the boundary region which readily dissolves but it absorbs by crystals when the crystals become activated by hydrolyzing in water.

CONCLUSIONS

The paper contains results from a laboratory investigation on the removal of heavy metal ions from water solutions by granular slag. The effect of pH, lead concentration, competing metal ions, slag particle size and contact time on the removal of lead in a column has been studied. The obtained result indicates that column process can be used for treating of waters containing relatively high lead concentrations as well as for selective removal of lead in the presence of other heavy metals. The effectiveness of the slag-packed columns with respect to heavy metal ions increases when a lower velocity and higher lead concentrations are used. In case of EAFS at low concentrations of lead, it was completely removed by slag after forty eight hours while, at high concentration of lead, much of the lead in the effluent water was absorbed at first thirty minutes of reaction while, leaching took place at longer times. When the absorbing bed was GBFS much of lead absorbs in the first thirty minutes of reaction but a few milligrams of it leached back into the solution. In both cases the absorbing bed were more effective for removing of higher concentrations of lead ions. The mechanism of lead removal in GBFS and EAFS column includes ion exchange/adsorption and precipitation.

Received : 24th July 2007 ; Accepted : 14th April 2008

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