

# Removal of Lead Ions by Various Types of Steel Slags

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**Abstract:** Steel slags are the by-products of steel industries, which are formed 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.

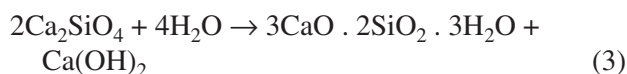
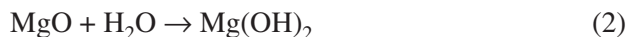
When Electric Arc Furnace Slag (EAFS) which is a basic crystalline slag was used in the presence of various concentrations of  $Pb^{2+}$ , ranging from 2 mg/l up to 10 mg/l, the  $Pb^{2+}$  ions were leached out into the solution and its concentration increased at the beginning of reaction but decreased dramatically 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 release was much lower compared to EAFS but the absorption of lead ions took place with the higher rates. Based on this research, if EAF slag was used as absorbing bed for reduction of lead ions in the industrial waters, it takes 24 hours to absorb 10 mg/l of lead ions, while if blast furnace slag was used, maximum amounts of lead was absorbed in the first thirty minutes of reaction.

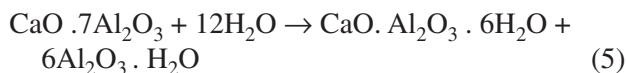
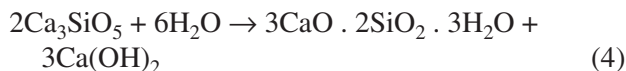
**Key words:** Granulated blast furnace slag, electric arc furnace slag, absorption of lead, atomic absorption spectroscopy.

## Introduction

Slags are the final wastes from the steel industry. Granulated blast furnace slag (GBFS) is generated during the iron production whereas the electric arc furnace slag (EAFS) is generated during a steel-manufacturing process by electric arc furnaces. In both type of furnaces, iron ore reacts with limestone and coke to produce molten iron. The slags, which are separated from molten iron and steel, are called GBFS and EAFS, respectively. 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 (Geiseler, 1996). Thus slag is currently considered as a product, and 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 (Geiseler, 1996; Li, 1999; Ramakrishina, 1997). 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 (Dimitrova, 2002; Mann, 1993; Ortiz, 2001). 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 follows (Yan, 2000):





Under the high pH condition, the slag surface is negatively charged and adsorbs cations, such as sodium and metal ions (Li, 1999; Ortiz, 2001). Dissolution of slag and adsorbed metal ions occurs with a condition of either low pH or high temperature (Ortiz, 2001). With the various pH environments the properties of slag may change and release of toxic elements may occur through the leaching process (Yan, 2000).

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 lead 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 (Patterson, 1985; Macchi, 1993). Sorption processes including ion exchange and adsorption are alternatives with great potential to treat water and wastewaters containing heavy metals (Ashirov, 1983; Groffman, 1992). 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 slags from ferrous metallurgy are complex mixtures of alkali-earth silicates and aluminosilicates formed at high temperatures in the blast furnace. Earlier research by Smith (2000) and Dimitrova (1998) 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 (1976), 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. (1983) 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 water 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 and water jet cooled (granulated), hence in the amorphous state, while electric arc furnace slag was produced by Mobarekeh steel company, and an air cooled slag in the crystalline form. Their chemical compositions analyzed by X-ray fluorescence are shown in Table 1. The X-ray fluorescence was Cambridge XR300.

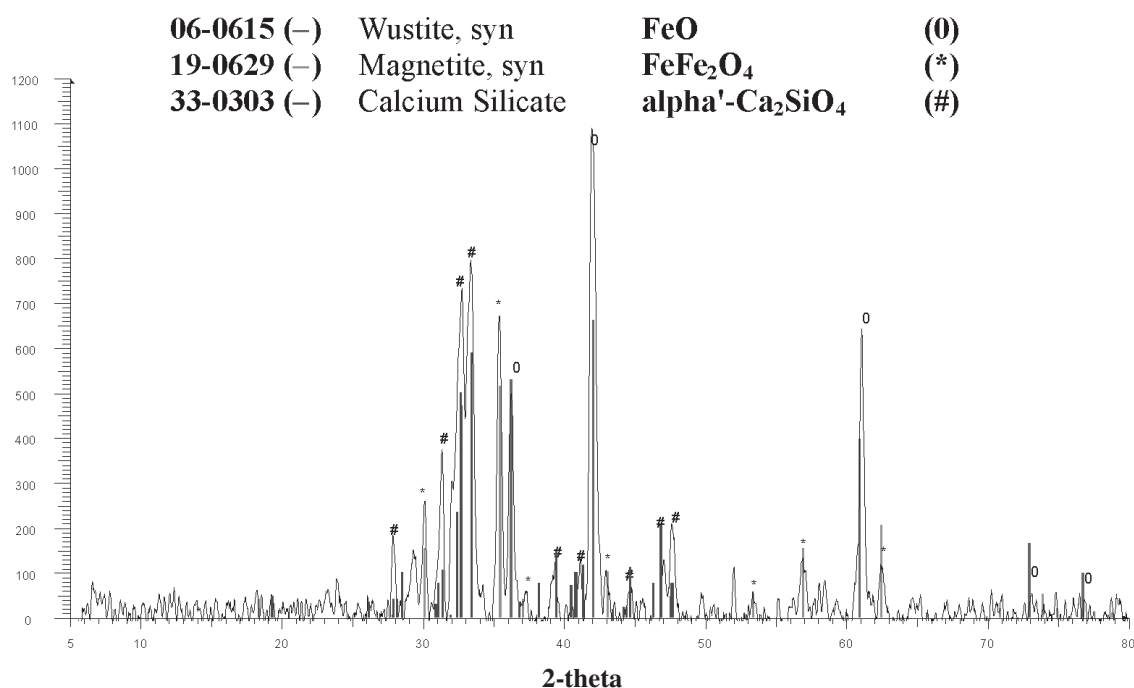
The mineralogy of slags were examined by a Philips Pw-1730 diffractometer using monochromatic Cu K and radiation. The X-ray spectra of the slags are shown in

**Table 1: Chemical composition of different steel slags**

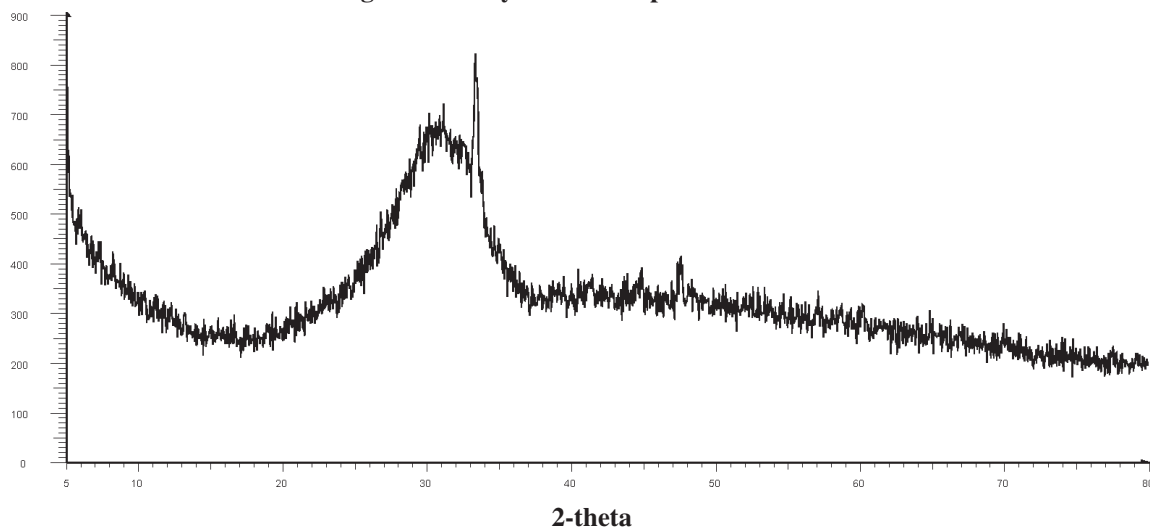
Chemical composition wt%	GBFS	EAFS
CaO	35.86-36.30	36-47
MgO	11.23-11.60	8-10
SiO <sub>2</sub>	36.51-36.21	14-16
FeO	0.90-0.50	25-30
Al <sub>2</sub> O <sub>3</sub>	9.95-9.98	5-8
MnO	1.1-0.71	1.1-2.5
S	1.07-0.86	0.04-0.065
TiO <sub>2</sub>	3.30-2.82	—
V <sub>2</sub> O <sub>5</sub>	0.08-0.07	—

Figures 1 and 2. The former is X-ray diffraction pattern of EAFS. According to this spectra, the slag is completely crystalline composed of crystals of wustite, magnetite and calcium-silicate, whereas the latter is the pattern of GBFS, showing 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 strength was ranged between 2 and 10 mg/l (ppm) based on the concentration of Pb. The pH measurements were made using a pH meter (TM-6). The concentration of metals were analysed 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 0.50–2.5mm). The apparent density was measured as 1.27 g/cm<sup>3</sup> and 1.29 g/cm<sup>3</sup> respectively. The slag bed height was 31 cm. The lead-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.



**Figure 1: X-ray diffraction pattern of EAFS.**



**Figure 2: X-ray diffraction pattern of GBFS.**

The stock solutions were prepared by using 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

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 that the slag can slowly release hydroxyl ions in the aqueous phase (Dimitrova, 2000). 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, 2002).

### 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 Figure 3. According to this result, when concentration of lead is low, much of it absorbs at first 30 minutes by steel slag, but after about two 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 set of experiments was done with the higher concentration of lead chloride which was 5 mg/l according to the concentration of lead. The results of this set of experiments are also graphically shown in

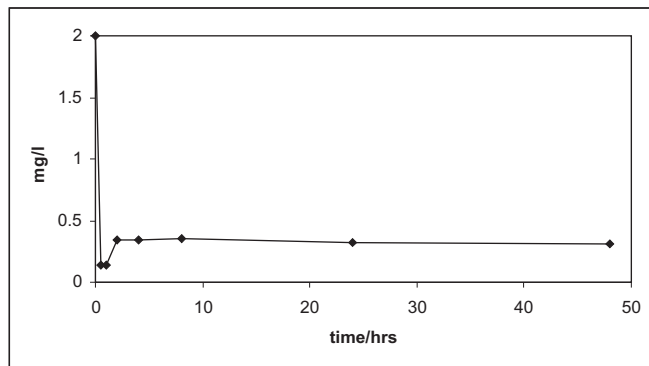


Figure 3: The effect of GBFS on 2 mg/l solution of  $Pb^{2+}$  ions.

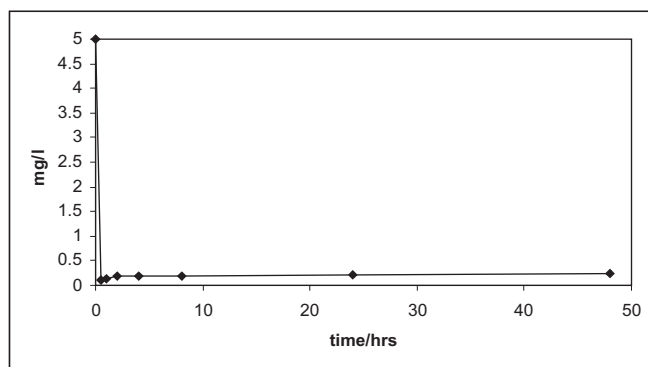
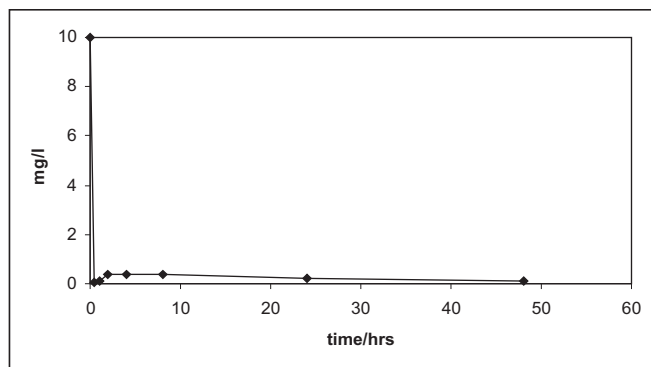


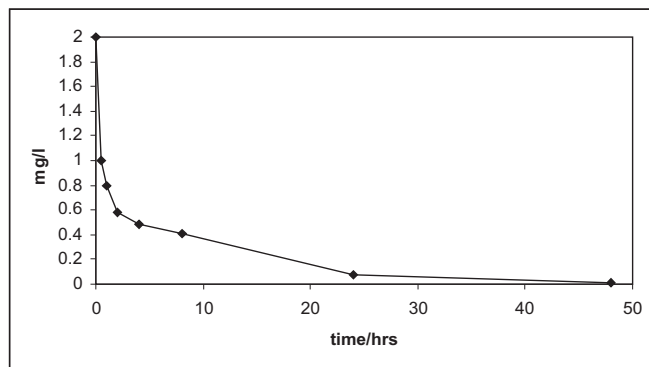
Figure 4: The effect of GBFS on 5 mg/l solution of  $Pb^{2+}$  ions.

Figure 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/l 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 Figure 5. Based on this figure, the amount of lead in the effluent water dropped 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 was absorbed by slag and its concentration dramatically reduced with the same trend up to 48 hours. It seems from the whole sets of experiments that lead ions absorb by steel slag dramatically and the amount of absorbing ion depends on the lead ion concentration of influent.



**Figure 5: The effect of GBFS on 10 mg/l solution of  $Pb^{2+}$  ions.**



**Figure 6: The effect of EAFS on 2 mg/l solution of lead ions.**

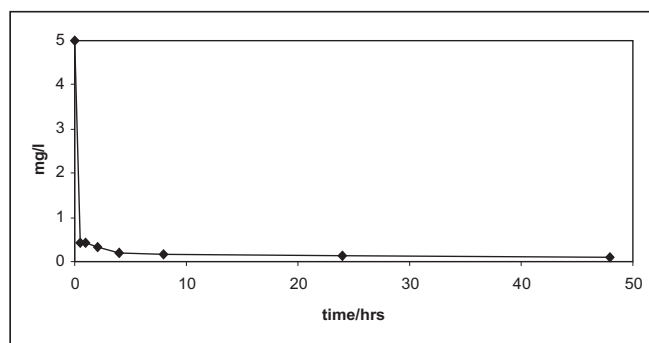
### The Effect of EAFS on Various Concentrations of Lead Solutions

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 two milligram per litre of lead ion passed over the absorbing bed, about fifty percent of it was absorbed during the first thirty minutes of reaction; the absorption continued but with lower rate. As it can be realized from Figure 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 were absorbed after forty eight hours of reaction.

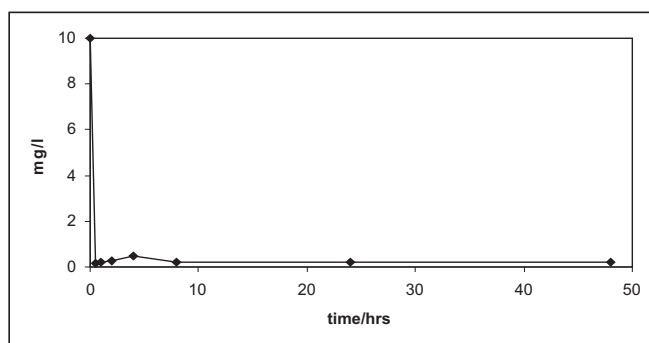
When higher concentration of lead such as 5 mg/l passed over EAFS, the concentration of lead dramatically dropped into 0.05 milligram per litre after thirty minutes, and stayed constant after one hour of reaction. Lead ions were absorbed by EAFS in a smooth rate at longer times and its concentration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

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

This behaviour of EAFS is possibly due to its crystalline mineralogical composition which is shown



**Figure 7: The effect of EAFS on 5 mg/l solution of lead ions.**



**Figure 8: The effect of EAFS on 10 mg/l solution of  $Pb^{2+}$  ions.**

by X-ray diffraction pattern in Figure 1. The total crystalline nature of this slag is due to the slow cooling process of it from the melt.

### 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 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 ( $\text{AlOH}$ ,  $\text{AlO}^-$ ,  $\text{SiOH}$ ,  $\text{SiO}^-$ ) is responsible for lead removal. Since the slag has more Si than Al, the silica surface sites should predominate. They are occupied by calcium and when GBFS is 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 they 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 water 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 in 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.

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