USE OF BY-PRODUCTS OF THE STEELMAKING INDUSTRY FOR REMOVING Pb²⁺ IONS FROM AQUEOUS EFFLUENTS

M.I. Martín¹, F.A. López² and F.J. Alguacil²

¹Eduardo Torroja Institute for Construction Science (CSIC). Serrano Galvache, 4, 28033 Madrid, Spain
²National Centre for Metallurgical Research (CSIC). Avda. Gregorio del Amo, 8, 28040 Madrid, Spain

Abstract

A study is made of the use of rolling mill scale and blast furnace sludge as adsorbents for removing Pb²⁺ ions from aqueous solutions. The adsorption of Pb²⁺ on these materials has been studied by the determination of adsorption isotherms. Different variables that affect the process (contact time, initial lead ion concentration and temperature) were evaluated. The adsorption processes are analysed using the Langmuir theory. Desorption processes for the metal from loaded by-products were also studied under several experimental conditions.

Keywords: Rolling Mill Scale, Blast Furnace Sludge, Lead, Langmuir Isotherms

INTRODUCTION

The effluents generated by industries generally have a complex composition which includes metals, suspended solids and other components [1]. According to increasingly stringent environmental laws, these effluents must be decontaminated because of their hazard to humans, animals and plants. Metals are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. High levels of lead in the blood in the infantile population are an important risk of mental slight delay and of increase of the arterial pressure. Also they can provoke changes in the conduct, as irritability, hyperactivity and lack of attention.

Different technologies have been proposed for the removal of metals, such as precipitation, ion exchange, solvent extraction, adsorption, cementation on iron, membrane processing and electrolytic methods [2-6]. The use of different industry by-products as adsorbent materials for the removal of metals from aqueous effluents has recently begun to be developed, with the aim of seeking alternative ways of recycling certain by-products and at the same time finding cheaper replacements for expensive conventional sorbent materials in different situations [2, 7-9].

Rolling mill scale is a steelmaking by-product from hot rolling processes which contains variable amounts of oil and grease. Spain generates about 44,000 t of mill scale every year [10]. The oil component in rolling mill scale makes its recycling difficult, and its direct reuse in sintering may lead to environmental pollution problems. Mill scale with a high oil content is recycled after extracting the oil in a pretreatment stage or is dumped. Coarse scale with a particle size of 0.5-5 mm and an oil content of less than 1 % can be returned to the sinter strand without any pretreatment [10].

Blast furnace sludge is another by-product of the steelmaking industry. Gases generated during the manufacturing of pig iron are cleaned prior to their emission into the atmosphere using any of several systems. When a wet process is used the effluent consists of a sludge, which is led to a Dorr thickener to increase its concentration. This study considers the concentrated sludge obtained from such a thickener. About 31,000 t of blast furnace sludge is produced in Spain every year [11].

In this work we have investigated the capacity of mill scale and sludge to remove Pb²⁺ ions, which may be present in liquid effluents.

EXPERIMENTAL

The mill scale was dried at 80 °C for 24 hours, revealing an initial moisture content of 5 %. The analysis of metallic iron was performed by titrating with a 0.1 N K₂Cr₂O₇ solution with barium
diphenylamine-sulfonate as indicator. For this determination the sample was first treated with a bromine-methanol solution, filtering of the residual oxides with a 20 mm crucible, with the Fe0 soluble in bromine-methanol passing into the filtrate [12].

The original sludge was a 57 % w/w suspension of solids in water. The suspension was vacuum-filtered and the resulting solid was dried at 80 °C for 24 hours before being crushed to yield a powder of a particle size of less than 40 μm. The chemical composition of the samples was determined by wavelength dispersion X-ray fluorescence analysis (WDXRF) using a Philips PW-1404 spectrometer.

Carbon and sulfur analyses in both cases were carried out by combustion in a Leco CS-244 oven and infrared detection.

The crystalline mineralogical composition of these samples was determined by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer (Cu Kα radiation).

The N2 adsorption isotherm was determined at 77 K for samples previously degasified at 60 ºC and 10-5 torr for 120 min, using a Coulter SA-3100 unit. The isotherm data was used to determine the BET specific area values of the materials studied.

For the removal of lead experiments the mill scale was passed through a screen, using only the < 0.5 mm fraction in the tests [9]. Pb2+ solutions were prepared by dissolving Pb(NO3)2 (chemical of reagent grade) in 0.01 M NaNO3, in order to maintain a constant ionic strength of the dissolution. 100 mL of the metal solution was added to 10 g of mill scale in Erlenmeyer flasks. Adsorption tests with the mill scale were performed using aqueous metallic solutions with concentrations varying between 0.015 and 3.0 g/L. On the other hand, 100 ml of the metal solution was added to 5 g of sludge. Removal tests with the sludge were performed using aqueous solutions with concentrations varying between 0.015 and 10 g/L.

The samples were kept in constant suspension by means of a thermostatically-controlled Lauda MS-20 unit at different temperatures (20 - 80 ºC) for an equilibrium time of 5 hours. The equilibrium pH was 5.0 ± 0.1. The pH was controlled using a Crison 517 pH-meter. The resulting suspensions were filtered and the solutions analysed by atomic absorption spectrophotometry (AAS) with a Varian SpectrAA-220FS spectrophotometer.

All experimental work used deionized water. The amount of metallic ion adsorbed on the mill scale and the sludge was determined by establishing the difference between the initial concentration and the equilibrium concentration.

RESULTS AND DISCUSSION

A. Characterisation of materials

Rolling mill scale has a laminar morphology and low specific surface area (S BET = 0.43 m2/g). It is composed mainly of a mixture of iron oxides: wustite (FeO), hematite (α-Fe2O3) and magnetite (Fe3O4), and metallic iron. Its iron content is Fe total = 68.20 % (Fe0 = 7.20 % (< 0.5 mm fraction)). Other elements are: Mn (0.48 %), Cu (0.47 %), Si (0.25 %), C total (0.21 %), Ca (0.13 %), Ni (0.11 %), etc. Approximately 2 % of mill scale is composed of oils and greases from the equipment associated with rolling operations.

Blast furnace sludge is a complex heterogeneous material with a specific surface area of 27.43 m2/g. Its morphology shows heterogeneity in the shape and size of the different particles. It is composed mainly of hematite (α-Fe2O3) and coke with minor quantities of wustite (FeO), magnetite (Fe3O4), maghemite (γ-Fe2O3), calcium ferrite (CaO⋅Fe2O3), quartz (SiO2) and calcium and aluminium silicates. Its iron content is Fe total = 33.00 %. Other elements are: C total (34.05 %), Fe (33.0 %), Si (3.65 %), Ca (2.30 %), Si (3.65 %), Zn (1.20 %), etc.

B. Adsorption experiments

B.1. Influence of temperature

Figure 1 shows the relationship between the different quantities of Pb2+ ions removed (or adsorbed) per unit of mass of adsorbent material and the equilibrium concentration of the metal ion at different temperatures for a reaction time of 5 hours. Tests were previously performed at different reaction times in order to determine the equilibrium time. The amount of Pb2+ removed per unit of mass of mill scale remains practically constant with temperature (Figure 1a). In Figure 1b is observed that all the sorption isotherms exhibit a similar shape. The
adsorption capacity of sludge increases with temperature.

**B.2. Adsorption isotherms**

Analysis of the relationship between adsorbent materials adsorption capacity and metal cation. Concentration at equilibrium was performed using the equations of Langmuir:

\[ \frac{C}{X} = \frac{1}{X_m} b + \frac{C}{X_m} \]  

(1)

![Figure 1. Mass of Pb²⁺ ions adsorbed per unit of mass of adsorbent material as a function of the cation equilibrium concentration in solution. t eq = 5 hours, (a) Mill scale, (b) Sludge.](image1)

where X is the amount of metal ion adsorbed per unit of mass of mill scale or sludge, Xₘ and a indicate the adsorption capacity of the adsorbent material, b and n are constants referring to adsorption intensity and C is the cation concentration at equilibrium.

The Langmuir isotherm is based on the assumptions that every adsorption site is equivalent and that ability of a particle to bind there is independent of whether or not adjacent sites are occupied [13].

Figure 2 shows Langmuir isotherms for the adsorption of Pb²⁺ in aqueous solution on mill scale and/or sludge at different temperatures. The metal solution concentration was varied and the reaction time was fixed at 5 hours. The Langmuir values Xₘ and b were calculated respectively as the slope and the C/X-intercept of each isotherm line at different temperatures and are shown in Table 1. The experimental results fit the Langmuir model well for both studied materials (R² ≥ 0.994 - mill scale and R² ≥ 0.990 - sludge).

![Figure 2. Langmuir isotherms. t = 5 hours, (a) Mill scale, (b) Sludge.](image2)

In Table 1 is observed also that the adsorption of Pb²⁺ on mill scale is practically independent of temperature and the adsorption capacity of this adsorbent material is very low (Xₘ = 2.74 mg/g - T = 60 °C) (Figure 3a); but the adsorption of metal on sludge is dependent of temperature (Figure 3b). The adsorption capacity of sludge rises

![Table 1. Langmuir parameters as a function of temperature](table1)

C. Desorption experiments

The resultant products of the adsorption process are products loaded with heavy metals and these residues cannot be incorporated into the sinter feed for recycling due to the fact that these might accumulate on the wall of the blast furnace and damage the refractories.

The stability of the loaded mill scale was studied for various times to assess the possibility of dumping the material in a landfill. In the experiment performed for a short time (leaching analysis) [14] mill scale loaded with Pb²⁺ (0.07 mg/g) was used and 200 mL of distilled water was added to 12.5 g of the loaded mill scale in an Erlenmeyer flask. The samples were kept in constant suspension at pH = 5.00 ± 0.01 (adjuste with acetic acid 0.5 mol/L) for 24 h. The results of the leaching analysis shows that the concentration of Pb ([Pb]leached = 0.3 mg/g, Pb_leached = 9.7 %) is less than the EPA limit [15] ([Pb]leached = 5.0 mg/g). Long times [12] stability experiment was carried out over 135 days at 20 ºC. Mill scales loaded with Pb²⁺ (1.00 mg/g) were used with 120 mL of distilled water added to 0.5 g of loaded mill scale in Erlenmeyer flasks. The test was carried out at pH = 5.00 ± 0.01 and pH = 3.00 ± 0.01 (adjusted with sulfuric acid 50 % v/v). The results show ([Pb]ₜₚₜ = 5.00 = 0 and [Pb]ₜₚₜ = 3.00 = 0.6 mg/L) that at pH 5.00
[Pb²⁺] under the experimental conditions studied is smaller than the limit defined by the Spanish Law 29/1985 [16] (legal limit = (0.5 - 0.2) mg/L). At pH = 3.0 both [Pb²⁺] is above their limits under the experimental conditions studied.

Previous studies [8] with loaded blast furnace sludge had proposed an alternative process to dumping because of its easily leached metal content. This process converts the loaded sludge into pellets using a disc pelletizer with a mixture of calcium carbonate, coke and bentonite [8]. The pellets obtained are then mixed with SiO₂ and heated to about 1000 °C in a controlled atmosphere in an electric furnace to release molten iron and the loaded metal together with a slag. The iron, with a purity of approximately 95-96 wt %, may be recycled in the steelmaking process [8]. This method avoids the dumping of a sludge which, because of its easily leached metal content, is a toxic and hazardous waste.

CONCLUSIONS

The removal of lead occurs through an adsorption process of Pb²⁺ on the surface of steelmaking industry material. The experimental results were well fitted, in each case, with the Langmuir isotherms. The adsorption processes of Pb²⁺ on sludge depend on the temperature, with the amount of adsorbed ions increasing as the temperature rises. In the case of adsorption process of Pb²⁺ on mill scale its adsorption is not dependent on the temperature. The data obtained shows that mill scale and sludge are effective sorbents of Pb²⁺ and perform well over a wide range of concentrations.

The treated by-products cannot be recycled in the steelmaking process because of their metal content. So these loaded by-products must either be treated to desorb the metals or dumped in a controlled landfill.

REFERENCES