

USE OF METALLURGICAL SLAG FOR THE REMOVAL OF B AND As FROM HIGHLY CONTAMINATED WATER RESOURCES IN TWO MEXICAN REGIONS: MECHANISMS AND EFFICIENCY

Rafael SCHOUWENAARS¹, Myriam SOLÍS-LÓPEZ¹, Elizabeth Diane ISAACS-PÁEZ², Bertha María MERCADO-BORRAYO², Rosa María RAMÍREZ-ZAMORA²

¹ Facultad de Ingeniería, Departamento de Materiales y Manufactura, Universidad Nacional Autónoma de México, Coyocacán, 01540, México.

² Instituto de Ingeniería, Coordinación de Ingeniería Ambiental, Universidad Nacional Autónoma de México, Coyocacán, 01540, México.

raf_schouwenaars@yahoo.com, rramirezz@iingen.unam.mx

Introduction

Acute shortage of usable water resources is one of the main obstacles for sustainable development in many regions worldwide. Optimal use of available resources, even when contaminated by geological or industrial processes is needed and development of new resources has to be considered. This paper presents a summary of work by the authors in which iron and steel slag were used for the removal of arsenic and boron present in geothermal waste water and As(III) and (V) present in groundwater.

Boron in geothermal wastewater and seawater is often treated by membrane processes, *e.g.* reverse osmosis (RO). Approximately 40–78% of the influent boron content can be found in the permeate in the case of seawater¹. Also in the case of geothermal water treatment, RO shows low removal efficiencies of B and As at high initial concentrations²⁻⁵. Ion exchange using commercial boron-selective resins combined with ultrafiltration shows a high efficiency and relatively low cost⁶ when compared to classical systems using only ion exchange with synthetic selective resins⁷. Drawbacks of combined systems in terms of process complexity, reagent consumption and cost have been reviewed by several authors^{8,9}.

Adsorption processes with commercial magnesium and iron adsorbents¹⁰ for the removal of As and B usually are expensive because of the high adsorbent doses required when initial concentrations are high. In addition, this process has not yet been evaluated for treating geothermal wastewater which has a complex composition. Various technologies have been developed for the removal of As, such as coagulation-flocculation¹¹, ion exchange^{12,13}, reverse osmosis^{14,15} and adsorption¹⁶⁻¹⁹.

Use of metallurgical slags is motivated by their high content of metal oxides, which have shown high adsorption capacity for metalloids¹⁶⁻¹⁹. This hypothesis is reinforced

by numerous studies using iron and steel slags for the adsorption of B^{20,21}, As²²⁻²⁴, phosphates^{25,26}, CO₂²⁷ and metals²⁸⁻³². Nonetheless, the specific surface area of the steel slag is 7.2 m²/g, the iron slag had an area of 0.3 m²/g. Other researchers report similar areas^{31,32}. This is an argument against adsorption as a removal mechanism.

Case studies

Preliminary screening of materials

An initial screening was performed analysing 5 slags: one came from a basic oxygen furnace for steelmaking, one from an electric arc furnace for steel making, one from an electric arc furnace for iron production, one from an electric induction furnace for steel and the last one from a blast furnace. The products were evaluated for chemical composition (XRF), mineral content (XRD), specific surface area and porosity (physical adsorption of N₂) and zeta-potential. Details of the experimental procedures and results were reported by Mercado Borrayo *et al.*²¹.

Removal tests were performed starting from initial concentrations of 700 mg/l B and residual B at equilibrium was determined by the spectrophotometric carmine method³³. Regression analysis provided the following relationship between the physicochemical characteristics of the slag and the residual B-concentration:

$$[B]_{eq} = 379 - 0.8 pZ - 29 \%MgO - 4.5 A_s \quad (1)$$

where pZ represents the zeta-potential and A_s the surface area. Other parameters were not significant. It is seen that for B-removal, Mg(OH)₂ is the principal determining factor, it was found independently that for As-removal, Ca(OH)₂ predominates. Based on these results, the BOF steel slag and the electric arc iron slag were selected for further research. The former contains 30% of portlandite and 38% of brucite as principal components, the latter contains 55% of maghemite and 31% Brucite.

Removal of As and B from geothermal wastewater

Wastewater from the “Los Humeros” geothermal field shows high contaminant levels (6 mg/L As and 600 mg/L B). International standards for wastewater treated for irrigation range from 0.1 to 2 mg/L As and from 0.5 to 15 mg/L B. Optimisation of the removal process was performed by means of a 2³ factorial design with central point with two replicates at each point, using commercial resins, iron nanoparticles and metallurgical slag (see Mercado Borrayo *et al.*²⁰ for experimental details). Response surfaces for slag and resin are compared in Figure 1. Maximal removal efficiency was 12% for As and 95% for B using resin, 95% for As and 94% for B using iron nanoparticles, 98% for As and 42% for B using steel slag and 96% for 62% for As and 86% for B with iron slag. A two-step process uses steel slag in the first step, removing 62% of As and 97% of B. In the second step, iron slag removes 95% of residual As and 40% of residual B. The product is an effluent containing 0.11 mg/L As and 10.6 mg/L B, within the limits for use in irrigation.

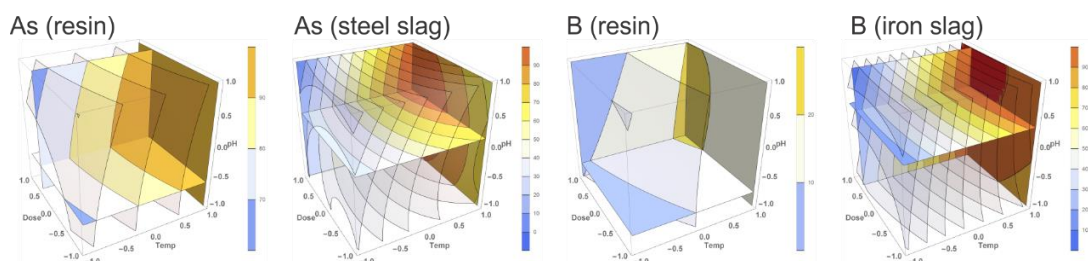


Figure 1: Removal efficiencies (%) of As and B with commercial resin and slag as a function of reagent dose, pH and temperature

Removal of As(III) and (V) from naturally contaminated ground water

The “el Muhi” well in Zimapán (20°44’45’’N 90°22’00’’W) is the most polluted by arsenic in Mexico^{34,35}, due to the abundance of As-bearing polymetallic veins in the surrounding limestone massif. Water resources are scarce in the region; the groundwater studied contains 1.26% As (V) and 0.23% As (III), the latter being the most toxic species. Additionally, the water contains high amounts of Ca, Mg, silicates, sulphates, fluorates and bicarbonates. Removal isotherms and kinetics were studied by varying slag dose and reaction times. The reactions were executed at a pH of 10 which is reached upon adding the slag to the contaminated water. A removal efficiency of 99% was reached with 4 g of steel slag after 120 sec. It was demonstrated that the removal process consists of the precipitation of the pollutant anions with Ca^{2+} dissolved from the slag (Figure 2). In contaminated groundwater, this process is accelerated as compared to laboratory solutions due to the common ion effect, instead of being inhibited by competition for available sites, as would be expected for adsorption.

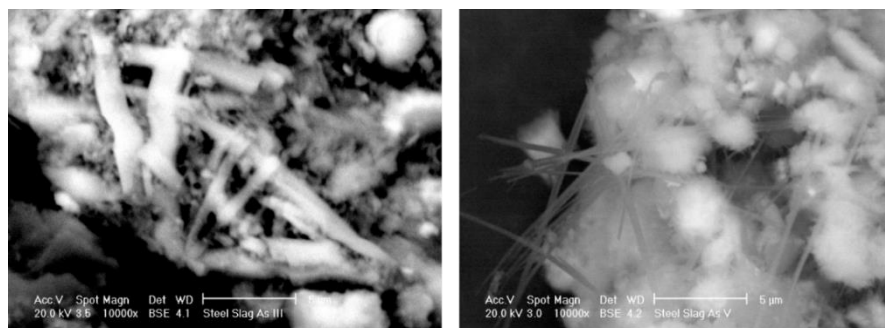


Figure 2: Precipitate morphology for As (III) (left) and As (V) (right) on steel slag

Conclusions

Metallurgical slags rich in Portlandite and Brucite are highly efficient for the removal of metalloids in high concentrations in naturally polluted water by means of a precipitation mechanism. They present an economical option for treatment under conditions where classical reagents fail. In the case of geothermal waste water, pollution levels were reduced to below the norm for irrigation; the As-levels in the groundwater of Zimapán could be brought to below the international norms for human consumption.

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