

Hexavalent chromium removal by ferrochromium slag

Mehmet Erdem^a, H. Soner Altundoğan^b, M. Deniz Turan^b, Fikret Tümen^{b,*}

^a Department of Environmental Engineering, Firat University, 23279 Elazığ, Turkey

^b Department of Chemical Engineering, Firat University, 23279 Elazığ, Turkey

Received 17 March 2005; received in revised form 20 June 2005; accepted 23 June 2005

Available online 10 August 2005

Abstract

The aim of this study is to demonstrate the potential of Cr(VI) generation during jigging operation applied for ferrochrome recovery from slag. The Cr(VI) concentrations of water contacted with ferrochromium slag (W/FS = 10) in a closed cycle after 50 batches were found as 0.61 mg/l. Also, reduction of Cr(VI) to Cr(III) and a subsequent precipitation of Cr(III) by using ferrochrome slag (FS) in a model solution has been aimed. The effects of amount of acid, contact time, FS dosage, initial Cr(VI) concentration and temperature on the Cr(VI) reduction have been studied through the batch runs. The amount of acid has been found to be the most effective parameter affecting the Cr(VI) reduction. A 10 g/l FS dosage and 3.5 ml/l H₂SO₄ (5 M) are sufficient to reduce all Cr(VI) in the model solution containing 10 mg/l Cr(VI) and for contact time of 60 min at 25 °C. In reduced solutions, precipitation of metal ions has been studied by using extra FS. A 60 g/l dosage of fresh FS can precipitate all Cr(III) and Fe ions in the reduced solution. Thus, it has been demonstrated that the treatment of jigging water stream to be generated in a ferrochrome plant containing Cr(VI) can be accomplished by using ferrochromium slag and sulphuric acid. Also, it has been determined that solid residues of the process are environmentally stable by applying TCLP test.

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Keywords: Hexavalent chromium; Reduction; Ferrochromium slag; Heavy metal removal; TCLP

1. Introduction

Ferrochromium is a master alloy of iron and chromium, containing 45–80% Cr and various amounts of Fe, C and other elements. Ferrochromium is produced pyrometallurgically by carbothermic reduction of chromite ore (FeO·Cr₂O₃). The main slag additives used are quartzite and aluminium oxide containing materials to compensate for the high magnesium content in certain ores, and magnesium and calcium oxide containing materials for aluminium rich ores. The ferrochromium slags consist mainly of SiO₂, Al₂O₃ and MgO in different phases such as spinel, MgO·Al₂O₃, and forsterite, MgO·SiO₂, but also smaller amounts of CaO, chromium and iron oxides and metal fragments. The chromium content in slags is 2–12%, in oxide and metal form. The slag/metal

amount ratio in smelting varies from 1.0 to 1.8, depending on raw materials [1].

Slag is discarded as a waste material in enormous quantities during the ferrochrome production. A relatively small percentage of this material finds application, but the vast majority of material generated each year is held in dumps and as land disposing costs increase, new disposal options are needed. As an alternative to land disposal, considering chemically inert and safe, slag has been used as construction materials and aggregate due to its excellent technical material properties [2–4].

Alternatively, reclaiming ferrochromium metal entrapped in slag seems to be economic. In order to recover metal, slag has been crushed and subjected to wet magnetic and gravimetric methods [1,5]. All of these might be good ideas, however, slags can contain high levels of extractable toxic elements which could pose environmental problem. In a study dealing with the process water of metal recovery from slag, it has been reported that Cr has been detected as chromate in

* Corresponding author. Tel.: +90 424 2370000/3643; fax: +90 424 2415526.

E-mail address: ftumen@firat.edu.tr (F. Tümen).

the processing water, which may create chromium pollution [6]. In another study, it has been reported that milling practice of ferrochromium slag could alter the oxidation state of chromium and cause the threat of Cr(VI) releasing [7]. On the other hand, it has been indicated that other solid wastes such as bag filter dust or its sludge produced during the ferrochromium production contain high levels of soluble hexavalent chromium [8–11]. Since these materials are considered as hazardous pollutants, their fixation and stabilization characteristics have also been studied [12–15]. The production of ferrochromium and stainless steel has been mentioned among the greatest contributors to atmospheric emission of chromium [16]. These facts show that ferrochromium production is a source of Cr(VI) pollution which can threaten the environment.

Chromium contamination of soil and water is a significant problem since hexavalent form of chromium is highly toxic, mutagenic and potentially carcinogenic to living organisms [17,18]. The most stable oxidation states of chromium are Cr(III) and Cr(VI) in aqueous systems. The trivalent chromium is quite immobile in the water environment because of limited solubility of its hydroxide, which is readily formed in the pH range of natural waters. Because of the benign character of Cr(III), detoxification and immobilisation processes of Cr(VI) is based on its reduction to Cr(III). Conventionally, the reduction of Cr(VI) is performed by using SO₂ and sulphite salts and ferrous sulphate in the treatment processes practised [19–22].

For hexavalent chromium treatment of ferrochromium recovery process water, FeSO₄ reduction and coke adsorption processes have been applied as a model solution [6]. In the mentioned study, chromium reduction properties of ferrochromium slag have also been found out. This fact brings to mind the idea that the treatment of jigging water containing Cr(VI) may be accomplished by using ferrochromium slag. It is worthy to investigate Cr(VI) reduction by using ferrochromium slag which contains iron and chromium mostly in metallic state as reductants. Further, oxide and silicate matrix of slag may partly adsorb chromates. Additionally, after reduction, in a following step another portion of slag may be used to neutralize the reduced solution in order to precipitate Cr(III) formed. That this waste has no cost and is readily available material in the ferrochromium plant may constitute an advantage. With economic point of view, in our earlier works, we have studied Cr(VI) reduction by some solid reductants such as copper smelter slag [23], steel wool [24], pyrite [25], synthetic iron sulphide [26] and siderite [27] which are cheap materials.

In this study, the use of ferrochrome slag for the reduction of Cr(VI) in the outlet water of ferrochrome reclaiming process was explored. For this purpose, firstly, chromium dissolution from ferrochromium slag contacted with water was tested. Then, amounts of sulphuric acid and ferrochromium slag on the reduction of Cr(VI) in a hypothetical model outlet water were studied.

2. Materials and methods

2.1. Material

2.1.1. Ferrochromium slag

Ferrochrome slag (FS) samples were provided from Elazığ Ferrochrome Plant of Etiholding (Turkey). FS was crushed to <1.2 mm (16 mesh). A portion of crushed FS sample was grinded and screened from a 200 mesh (75 μm) screen. Both FS samples (<16 and <200 mesh) were used for obtaining model outlet water of jigging. Less than 75 μm fraction (<200 mesh) of FS was used for Cr(VI) reduction study. The XRF analysis of FS sample was given in Table 1.

2.1.2. Cr(VI) solutions

A 1 g/l Cr(VI) stock solution was prepared by using K₂Cr₂O₇. All working solutions in different concentrations were prepared by diluting the stock solution with distilled water.

2.2. Methods

2.2.1. Model of jigging outlet water

A 5 l of tap water was mixed with 500 g of crushed original FS sample [W/FS ratio (w/w) = 10]. This mixture was reciprocally shaken for 2 h. The water was separated from solid by decanting. The water obtained at washing operation was mixed with a fresh portion of FS in the ratio of 10. This mixture was shaken for 2 h. A 50 ml water sample was pipetted at the end of each fifth batch. This procedure was sequentially repeated 50 times by keeping the W/FS ratio of 10 and contact time of 2 h. Water samples drawn at every fifth stage were subjected to pH measurements and Cr(VI), total Cr and Fe analyses. This test was also repeated for grinded FS sample.

2.2.2. Hypothesis of reduction process

Our preliminary tests showed that Cr(VI) could be reduced in the aqueous solution by slag in acidic conditions. The reduction of hexavalent chromium by metallic components of slag in acidic solutions can be expressed by following equation:

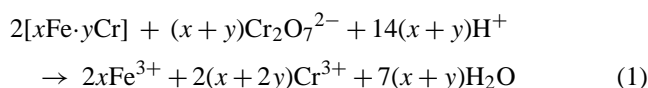


Table 1
Chemical composition of ferrochromium slag (FS) sample

Constituent	%
Fe	1.40
Cr	5.20
SiO ₂	28.89
Al ₂ O ₃	29.64
MgO	31.51
CaO	0.50

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