VERSATILE MEDIA TO REMEDIATE SITES CONTAMINATED BY CHROMIUM USING A SYSTEM OF PERMEABLE REACTIVE BARRIERS

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ABSTRACT – The use of permeable reactive barriers (PRB) has been drawing the attention of researchers for groundwater contaminations. Searching for a new material capable to reduce hexavalent chromium, this work proposes the application of a steel waste (BFD) as reactive media to reduce and precipitate chromium in loco. Batch tests wore developed in order to check the applicability of the residue on the reduction process. Results of batch tests showed that BFD can reduce up to 60% of hexavalent chromium on solution.

1. INTRODUCTION

Natural occurring due to rocks composition, or wrongly disposed from industrial activities, hexavalent chromium is a important problem on groundwater, and deserves attention because is carcinogenic according to International Agency for Research on Cancer (IARC, 1990). Although hexavalent chromium represents a risk, trivalent chromium is an atoxic micronutrient, and a less mobile compost due to its capacity to form insoluble hydroxides. Environmentally speaking reduce Cr VI to Cr III is a great remediation for groundwater.

Remediation technologies for groundwater usually involve pump water, treat it outside of soil and then pump the water again to soil. The pump & treat technologies requires a large amount of power and high cost. Looking forward for alternative techniques, permeable reactive barriers (PRB) has been drawing the attention of researchers because of the facility and low operational (EPA, 1998). The technique consist in introduce a reactive media in the soil, perpendicularly to the groundwater flow, expecting the reaction (contaminant degradation, precipitation and sorption) of this material with the present contaminants (THIRUVENKATACHARI, 2007) as can be observed on Figure 1.

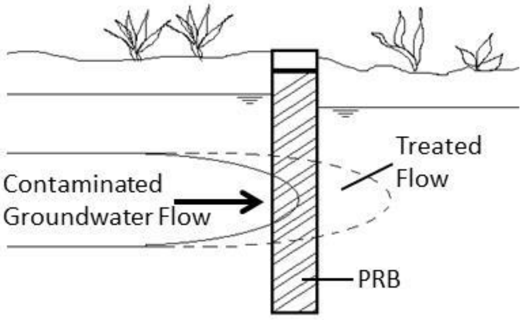

Figure 1 – Schematic system for a permeable reactive barrier. Adapted from Gavaskar (2000).

In the case of hexavalent chromium remediation, PRB systems can be used introducing a reactive media capable to reduce Cr VI to Cr III. Thiruvenkatachari (2007) studied 124 PRB projects in US, and related that 45% of those projects proposes iron as reactive media.

For chromium reduction, iron can react as showed in Equations 1 and 2 (EPA, 1998; BLOWES, 1997):

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O \qquad (1)$$

$$Cr^{6+} + 3Fe^{2+} \rightarrow 3Fe^{3+} + Cr^3 \qquad (2)$$

The PRB construction can involve the use of hundreds tons of reactive media, and this factor can prohibit economically the use of several studied compounds that technically showed good results.

Looking for alternative reactive media, this work proposes the use of a steel waste, rich in iron and carbon. According to the Sustainability Report of Brazil Steel Institute (2013), the country has generated the amount of 17.1 million tons of steelmaking wastes in 2012. 11% of these wastes can’t return to the process due to its chemical characteristics or particle size distribution, being stocked or destined to landfill. Among these steelmaking wastes, we can find the Blast Furnace Dust (BFD), that presents a high percentage of iron in its composition, and showed good results for Cr(VI) reduction (AMORIM, 2013) in batch systems.

2. METHODOLOGY

For the characterization were realized the following analyses: ray-x diffraction (Diffractometer, model PW1710, CuK a = 1.54051 Å; graphite crystal monochromator, scan rate of 0,06º 2θ/s), that was held for the identification of the iron crystalline stages present on BFD. For the identification and quantification of the stages of presents iron on residue, was used the Mossbauer spectroscopy technique (57CO font in Rh matrix, using α– Fe as standard).

The batch tests, were held in flasks, where were added 5g of samples of steel waste in suspension in 50 ml of a $K_2Cr_2O_7$ solution with a concentration of 50 mg/L of Cr(VI). Samples were analyzed for the presence of Cr(VI) by the colorimetric method of diphenylcarbazide. The 1.5-

diphenylcarbazide reagent, complex with hexavalent chromium in acidic pH, forming a solution which can be measured by visible spectrophotometry (540 nm) (spectrophotometer UV – 1650 PC, Shimadzu).

In order to check if a previous acid washing was necessary, we performed a batch test on three different pretreatments:

1) 5 grams of BFD washed with acid solution (3 M), pH of reaction was 6.8→10 mL of HCl was added, and after the agitating, the solution was discarded, and the residue was washed with 20 ml of deionized water by 3 consecutive times. On second rinse the pH was raised to 7 to avoid possible interference of low pH on the reduction of Cr (VI)

2) 5 grams of BFD washed with acid solution (3 M), pH of reaction was 2.8 →10 mL of HCl was added, and after the agitating, the solution was discarded, and the residue was washed with 20 ml of deionized water by 3 consecutive times, with no pH adjustments.

3) 5 grams of BFD washed with water (3 M), pH of reaction was 7 → The residue was washed with deionized water and no pH adjustment.

3. RESULTS

3.1. *Steelmaking Waste Characterization*

According to the preliminary characterization by Amorim (2013), presented on Table 1, it's possible to note that the residue used has a superficial area relative low. It is a very thin powder, with predominance of mesopores and has an elevated zero charge point (zcp).

Table 1-Characterization of BFD (AMORIM et al, 2013)

Steelmaking waste BFD	
Parameter	**Values**
Area (BET) ($m^2.g^{-1}$)	3.4
Total pore volume ($cm^3.g^{-1}$)	$1.11x10^{-3}$
Pore diameter (nm)	13.2
Particles size	99.6 % < 75 µm
pH zcp	10
X-ray fluorescence	
-Majoritarian elements:	Fe, O
-Minoritarian elements:	Si, Al, S, P, Mg
-Trace elements:	Mn, Cr, Ti, V, Ca, K, Cl, Na

X-ray diffraction analysis of the BFD waste (Figure 2) indicated the presence of hematite α-Fe2O3 (2θ at 28.2, 38.8, 41.8, 48.0, 58.3, 63.9, 74.0, 76.2°) and a spinel structure (2θ at 20.8, 35.3, 40.9, 42.7, 50.03, 62.4, 66.4, 73.3°) related to the presence of Fe_3O_4 magnetite.

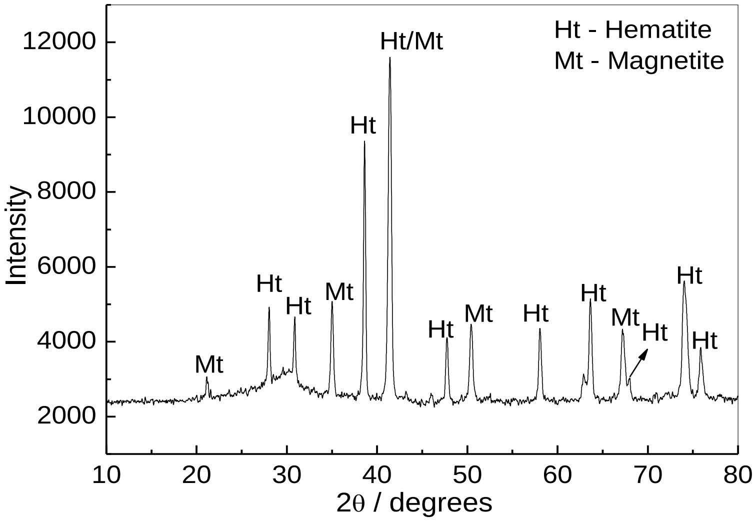

Figure 2 – Powder X-ray diffraction of BFD (Ht=hematite and Mt=Magnetite).

The results of the iron species distribution by Mössbauer analysis indicated the presence of maghemite (7%), hematite (51%) and magnetite (42%), with tetrahedral site [Fe_3O_4] and octahedral sites {Fe_3O_4} (Figure 3).

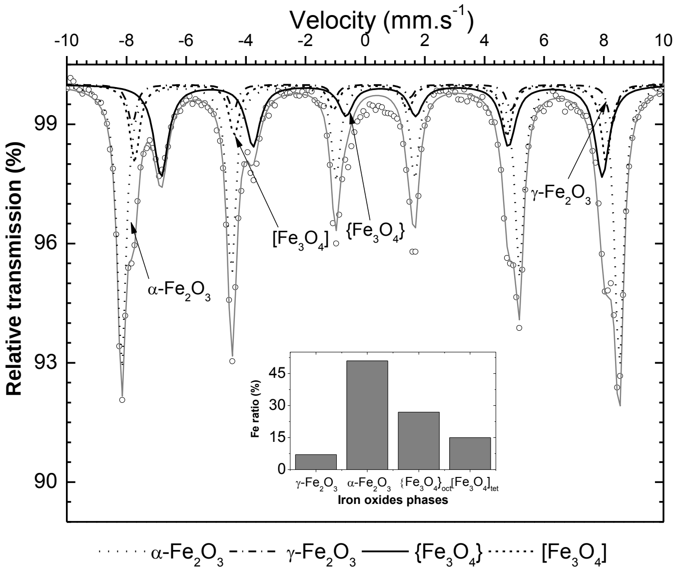

Figure 3 – Mössbauer spectra and iron phase distribution for BFD.

As can be observed on mössbauer spectra, around 50% of the iron from this steel waste can be considered magnetic. For the proposal of this study, BFD is an interesting material due to the high amounts of iron. As shoed on X-ray and Mössbauer spectra, the iron present on the steel waste is Fe II and Fe III. The first one can reduce hexavalent chromium, as showed on Equation 2.

3.2. Batch Tests

Several studies indicate that acid washing from iron eliminates the presence of a possible oxidized layer, exposing the most reactive materials and providing greater effectiveness in reducing process (THIRUVENKATACHARI, 2007; MAGALHÃES, 2012). Due to this, previous tests were performed to decide if acid washing was necessary.

Three batch tests were realized to compare the following conditions: water washing (washed with water, and reactional pH = 7); acid washing (washed with acid, and reactional pH = 6.8) and acid washing (washed with acid, and reactional pH = 2.8). The results from of these preliminary tests can be observed at Figure 4.

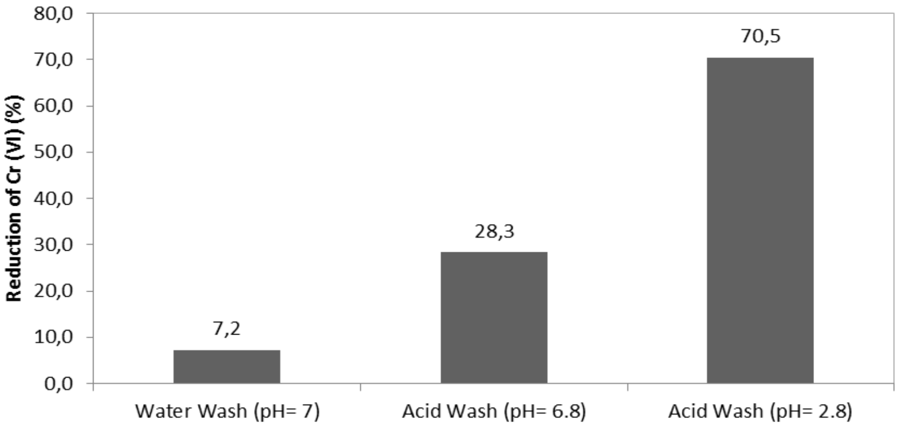

Figure 4 – Results from previous tests comparing different pretreatments to BFD.

Previous acid wash showed to be an interesting way to improve BFD capacity to reduce hexavalent chromium. As can be observed, the pH value during the test also interferes, and acid wash plus low pH values can reduce up to 70% of chromium in solution.

Figure 5 presents the reduction process during the time, at the best operational conditions (acid wash and pH = 2.8).

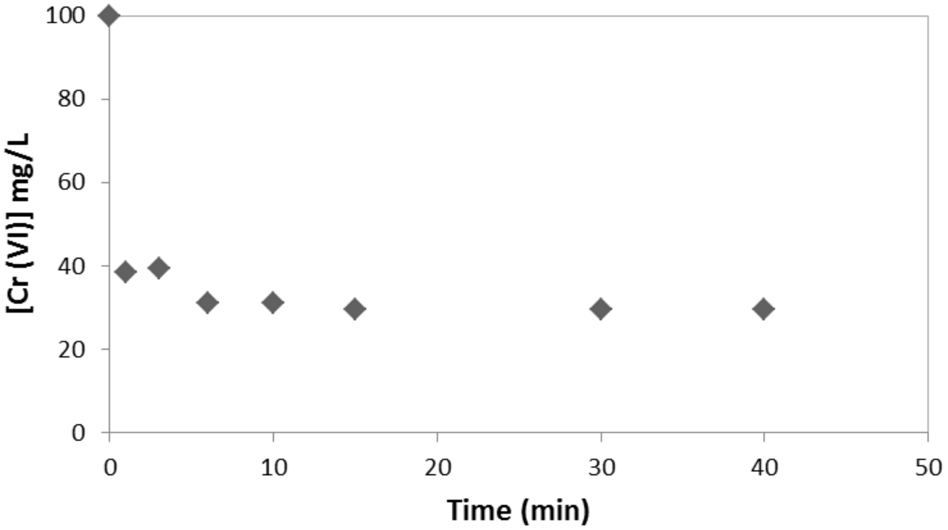

Figure 5 – Hexavalent chromium reduction during the time using BFD at pH= 2.7 (washed with acid medium).

Result of Figure 5 show that reaction occurs at the first minutes, that the process is capable to reduce 70% of the Cr (VI) on solution, and that each gram of BFD can reduce 0,3 mg of Cr (VI).

According to the results, BFD can be used as a reactive media to reduce hexavalent chromium in PRBs systems. The mechanism that reduces Cr (VI) is described at Figure 6. As showed, Cr (VI) reacts with Fe2+ from the steel waste, oxidizing it to Fe3+. The trivalent chromium formed can react with Fe3+ and adsorb or precipitate.

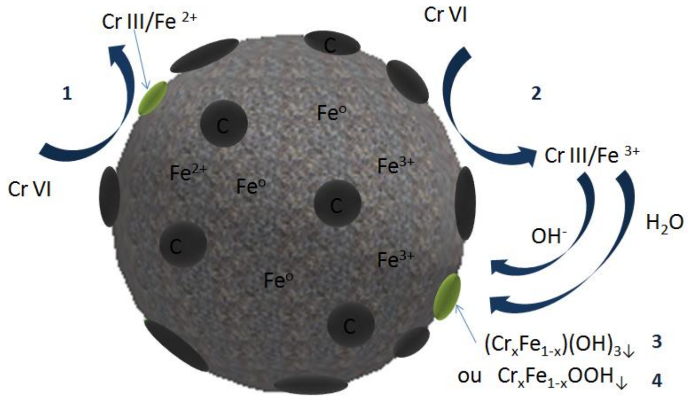

Figure 6 – Mechanism proposed for hexavalent chromium reduction using BFD as reductor agent.

4. CONCLUSIONS

The presented research shows us that Blast Furnace Dust has a capacity to reduce hexavalent chromium. More research is needed to define specific parameters for the use of this residue as reactive media on PRB systems, but the implementation of the proposed system associates the destination of a stocked waste, and a cut of cost on a groundwater remediation technology.

5. ACKNOWLEDGEMENT

The authors thank the Foundation for Research Support of the State of Minas Gerais – FAPEMIG and CNPQ for the financial support, and also the chemical analysis laboratory of the department of metallurgical engineering from the Federal University of Minas Gerais.

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