Waste Management 34 (2014) 2687–2696

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Simultaneous recovery of vanadium and nickel from power plant fly-ash: Optimization of parameters using response surface methodology

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ARTICLE INFO

Article history:
Received 20 April 2014
Accepted 25 August 2014
Available online 27 September 2014

Keywords:
Power plant fly ash
Hazardous
Vanadium
Nickel
Acidic leaching
Response surface methodology

ABSTRACT

Simultaneous recovery of vanadium (V) and nickel (Ni), which are classified as two of the most hazardous metal species from power plant heavy fuel fly-ash, was studied using a hydrometallurgical process consisting of acid leaching using sulfuric acid. Leaching parameters were investigated and optimized in order to maximize the recovery of both vanadium and nickel. The independent leaching parameters investigated were liquid to solid ratio (*S*/*L*) (5–12.5 wt.%), temperature (45–80 °C), sulfuric acid concentration (5–25 v/v%) and leaching time (1–5 h). Response surface methodology (RSM) was used to optimize the process parameters. The most effective parameter on the recovery of both elements was found to be temperature and the least effective was time for V and acid concentration for Ni. Based on the results, optimum condition for metals recovery (actual recovery of ca.94% for V and 81% for Ni) was determined to be solid to liquid ratio of 9.15 wt.%, temperature of 80 °C, sulfuric acid concentration of 19.47 v/v% and leaching time of 2 h. The maximum V and Ni predicted recovery of 91.34% and 80.26% was achieved.

1. Introduction

Fly ash is a solid residue which is collected in off-gas treatment system of power plants using heavy fuel oils. This residue is an important secondary resource for vanadium after primary resource of the ore concentrates and the metallurgical slag (Xiao et al., 2010). The production of these fly ashes is of environmental concern (Tsai and Tsai, 1998; Al-ghouti et al., 2011). Thus, recovery of vanadium and nickel from heavy fuel fly ash is important from the viewpoint of reclamation of vanadium and nickel which are considered as one of the most hazardous metal species creating serious hydrometallurgical problem in terms of environmental conservation (Amer, 2002). Recovery of vanadium and nickel from this ash is also of economical concern. The fly ash deriving from heavy fuel oil combustion contains appreciable levels of vanadium (up to 13 wt.%) and nickel (up to 7 wt.%) in highly leachable forms that makes their recovery interesting (Abdel-latif, 2002).

Vanadium is usually found in ores, concentrates, metallurgical slags and petroleum residues. Vanadium and nickel have many and continuously increasing industrial applications (Vitolo et al., 2001; Tsygankova et al., 2011). Among the compounds of vanadium in the fly ash, vanadium pentoxide, V_2O_5, and vanadic oxide, V_2O_4, are slightly soluble in water but dissolve easily in acid and alkaline solutions (Abdel-latif, 2002). Nickel is an important metal applied in many fields, such as energy materials and functional materials, chemicals and catalysts, cathodes, batteries and it has several metallurgical benefits such as high melting point, ferromagnetic properties and ease of electroplating (Al-Mansi and AbdelMonem, 2002). Hydrometallurgical processing is usually found as the preferred route for the recovery of vanadium and nickel from the fly ash, due to the relatively low operating and energy costs (Tsai and Tsai, 1998).

T-sai et al. (Ognyanova et al., 2009) reported a two-stage leaching method, applicable to recovery of nickel, vanadium and ammonium sulfate from fly ash. Amer (Amer, 2002) worked on the hydrometallurgical processing that involved acid leaching under oxygen pressure of ground ash, followed by electrolytic separation of nickel from sulfate solution and vanadium was then neutralized and precipitated by adjusting pH and calcined to produce V_2O_5. Abdel-latif (Xiao et al., 2010) reported a developed process flow sheet used as a basis to identify the test work required for the major processing units. The flow sheet consisted of drying, de-carburization and desulfurization stages, followed by a smelting stage at the end. In another study, extraction of vanadium from heavy fuel oil fly ash was performed using a burning stageto reduce the carbonaceous fraction, followed by acid leaching and oxidative precipitation of vanadium pentoxide (Khorfan et al., 2001). The advantage of this approach over the direct leaching of the raw fly ash is the reduced volume of a more concentrated residue as a feed entering

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http://dx.doi.org/10.1016/j.wasman.2014.08.021
0956-053X/

to the vanadium recovery process. According to Tsygankova et al. (Mahdavian et al., 2006) there is no single approach to directly recover vanadium from various ashes and each ash needs its own leaching procedure depending on its chemical and phase compositions. Navarro et al. (Al-ghouti et al., 2011) used leaching processes (acidic and alkaline treatments), followed by a second step of metal recovery from leachates involving either solvent extraction or selective precipitation.

In order to decrease the number of experiments, design of experiments (DOE) can be used. Optimization using response surface methodology (RSM) is the best method of optimization for hydrometallurgical processes because of two main reasons: first, suitable precise results obtained and second, determination of interactions between the effective parameters (Hamzaoui et al., 2008). Determining the optimum conditions to maximize the recovery is of great importance which is also the subject of the current study. Current optimization methods in use are not effective enough, as they only consider one parameter at a time which means that interaction between parameters is ignored. In order to overcome this problem, RSM has been considered recently (Hamzaoui et al., 2008; NaseriJoda and Rashchi, 2012). The central composite design (CCD) has been used to collect the data for fitting the second order response.

The objective of the present paper is to establish the optimum conditions (solid to liquid ratio (*S*/*L*), leaching temperature, acid concentration, and reaction time) for maximum recovery of both vanadium and nickel from fly ash by means of sulfuric acid leaching using analysis of variance (ANOVA). Optimization of vanadium and nickel recovery using RSM method was also determined.

2. Experimental

2.1. Materials

The fly ash sample was a mixture collected from different power plant stations in Iran which use oil as fuel. Sulfuric acid (H_2SO_4) used in the leaching was obtained from Merck, with a purity of 96–98%. Ammonium iron (II) sulfate $(NH_4)_2Fe(SO_4)\cdot 6H_2O$, ammonium persulphate $(NH_4)_2S_2O_8$ and potassium permanganate ($KMnO_4$) used for titration test were 99% pure from Merck.

2.2. Preparation

Different fly ash samples were mixed crushed and a portion was taken by quartering. The selected portion was then crushed to a smaller size and divided again. This procedure was repeated and the sample was sieved to obtain −75 μm size fraction.

2.3. Characterization

The sample prepared for the recovery process was digested in sulfuric acid and analyzed by inductive couple plasma (ICP-OES) using a VISTA-PRO (VARIAN, Australia) instrument. The chemical analysis of the sample was determined and shown in Table 1. As seen in this table, the fly ash contains 14.43% V and 5.19% Ni which is high as compared to other plants. Carbon, hydrogen and nitrogen in the fly-ash were determined by a LECO CHN-600 (model CHN-600 from Germany) elemental analysis. Mineralogical and chemical analyses of the sample were done using X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF). The XRD pattern is shown in Fig. 1. The XRD result revealed that the fly ash is totally amorphous and no specific peak was observed. Table 2 presents the chemical analysis of the sample obtained from XRF. To measure the concentration of vanadium and nickel in the leach solutions, ferrous ammonium sulfate titration method was used (Moghaddam et al., 2006). In order to check the titration results, some samples were also analyzed by both atomic absorption spectroscopy (AAS) (Shimadzu AA670) and ICP. The difference between titration results and the other two methods was determined to be less than ca. 4%.

Table 1
Chemical analysis of the fly ash determined by inductive coupled plasma analysis (ICP-OES).

Component	V	Ni	H[a]	N[a]	C[a]	S	Cr	Ge	Ga
Content (wt.%)	14.43	5.19	1.16	0.47	13.07	2.6	0.116	0.018	1.044

[a] *C, H and N content obtained by a LECO CHN 600 analysis.*

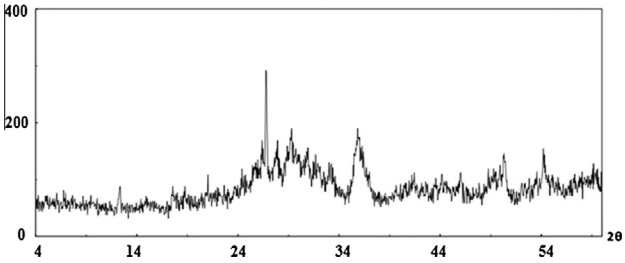

Fig. 1. The X-ray diffraction (XRD) pattern of the sample.

2.4. Acid leaching

In a typical leaching test, 30 g of the sample was leached in sulfuric acid solution at the condition of: liquid to solid ratio (5–12.5 wt.%), temperature (45–80 °C), sulfuric acid concentration (5–25 v/v%) and time (1–5 h), as listed in Table 3. The leaching reactor had three necks, one for the condenser, one for the thermometer and the last one served either for the inlet of the sample or for withdrawal of samples at regular time intervals. The reaction mixture was agitated with a magnetic stirrer and heated on hot plate indirectly through a water bath. After a certain leaching time a Buckner funnel equipped with a glass filter was used for filtration. The slurry was filtered and the filtrate was analyzed for both V and Ni by titration (Moghaddam et al., 2006).

2.5. Leaching experimental design

To obtain the optimum operating conditions an empirical model was developed. The applied optimization approach was based on a central composite design and response surface methodology. In general, central composite design requires a total of $(2^k + 2k + N_0)$ runs where k is the number of studied factors, 2^4 are the points from the factorial design, $2k$ the face-centered points and N_0 the number of experiments carried out at the center (NaseriJoda and Rashchi, 2012; Khuri and Mukhopadhyay, 2010). Duplication of the center points was used to determine the experimental error. In current study, 2^4 factorial design was used and six ($N_0 = 6$) central replicates were also employed. The experiments were carried out in random order to minimize the effect of systematic errors. Thirty experiments were performed corresponding to the four variables of the central composite design; the parameter levels and response value (V recovery and Ni recovery) are given in Table 4. Following the experimental design, the samples were analyzed to determine their vanadium and nickel contents using titration. The DESIGN EXPERT 8.0.1 trial version (State-Ease Inc., Minneapolis, MN, USA) software was used for regression and graphical analysis of the obtained data.