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Direct recovery of boiler residue by combustion synthesis

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ABSTRACT

Boiler residue (BR) of thermal power plants is one of the important secondary sources for vanadium production. In this research, the aluminothermic self-propagating high-temperature synthesis (SHS) was used for recovering the transition metals of BR for the first time. The effects of extra aluminum as reducing agent and flux to aluminum ratio (CaO/Al) were studied and the efficiency of recovery and presence of impurities were measured. Aluminothermic reduction of vanadium and other metals was carried out successfully by SHS without any foreign heat source. Vanadium, iron, and nickel principally were reduced and gone into metallic master alloy as SHS product. High levels of efficiency (>80%) were achieved and the results showed that SHS has a great potential to be an industrial process for BR recovery. SHS produced two useful products. Metallic master alloy and fused glass slag that is applicable for ceramic industries. SHS can also neutralize the environmental threats of BR by a one step process.

1. Introduction

Vanadium, Nickel, and Iron are the major valuable metallic elements in crude oil that accumulate in boiler ash and fly ash after burning (Navarro et al., 2007). In addition to economical futures, the recovery of these waste materials has environmental importance and prevents above mentioned metals from releasing in nature (Vitolo et al., 2000).

Boiler and fly ashes were hydrometallurgically recycled by acidic or alkaline leaching solutions (Akcil et al., 2015; Akita et al., 1995; Tsai and Tsai, 1998). Leaching of fly ash and boiler residue in alkaline solutions like Na_2CO_3 (Al-Ghouti et al., 2011), NaOH (Al-Zuhairi, 2014; Chmielewski et al., 1997; Tsygankova et al., 2011), and KOH (Guirguis et al., 2014) has resulted to a highly selective leaching of vanadium besides depressing Ni and Iron dissolving. Furthermore High-temperature roasting of boiler residue with Na_2CO_3 and leaching in hot water can only solve vanadium (El-tawil et al., 1992). In the case of acidic leaching, all metallic elements had entered to the leachant and different purification processes are needed for extraction of pure products (Amer, 2002; Barik et al., 2014; Nazari et al., 2014; Vitolo et al., 2001). In recent years, bio-leaching has used successfully to leach elements V, Ni from powder plants boiler residues (Coman et al., 2013; Rasoulnia et al., 2016; Rasoulnia and Mousavi, 2016a, 2016b). All hydrometallurgical processes leave solid wastes that contain all primary metallic elements but in smaller amounts. These wastes are still threatening the environment. The pyrometallurgical process can produce by-products that never release metallic elements.

As an example of pyrometallurgical recovery of vanadium bearing residues, fly ash was heated to release carbon and sulfur and then was heated to 1600 °C in an induction furnace and metallic elements were reduced by aluminum or ferrosilicon (Abdel-Latif, 2002). Reduction of vanadium is possible via carbon, silicon and aluminum. Existing carbon in a petroleum fly ash has employed to reduce vanadium of fly ash and iron of steelmaking flue dust to produce ferrovanadium (Xiao et al., 2010a, 2010b). However carbon is not acceptable mentioned as a satisfactory reducing agent because carbothermic products have high carbon amounts (Gasik et al., 2009). Boiler ash has been directly treated in the electro-silico-thermic process for ferrovanadium production (Bauer et al., 2005). The aluminothermic reduction is one of self-propagating high-temperature synthesis (SHS) processes that metallic aluminum reduces mainly transition metals and can be used for production of pure metals, and metals compounds as well as ferroalloys (Kamat and Gupta, 1971; Munir and Anselmi-Tamburini, 1989; Yücel et al., 1996; Ziatdinov and Shatokhin, 2010). Vanadium oxide can be reduced by aluminum in an electrical arc furnace or in magnesia-lined vessel (thermite reaction) to produce ferrovanadium (Baroch, 2005; Bauer et al., 1997).However, no report has released about the aluminothermic processing

Abbreviations: BR, boiler residue; SHS, self-propagating high-temperature synthesis; XRF, X-ray fluorescence; XRD, X-ray diffraction; SEM, scanning electron microscope; BS-SEM, back scattered scanning electron microscopy.

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of BR. The objective of this research was examination and evaluation of aluminothermic reduction for BR recovery.

2. Material and methods

The chemical composition of primary BR that has analyzed by X-ray fluorescence (XRF) is listed in Table 1. Vanadium, Iron, and Nickel are the three target transition metals in BR that can be reduced by aluminum. The X-ray diffraction pattern (XRD) of BR demonstrated that mixed oxides were dominant phases i.e. NaV_3O_8, $Na_5V_{12}O_{32}$, $Na_{10}V_{24}O_{64}$, $Na_XV_2O_5$, $Ni_2Fe_3V_3O_{11}$, and $Na_2Ca(VO_3)_4$. All Vanadium bearing phases had the general formula of $(Na_2O)_xV_2O_5$. Nickel and iron had participated in forming the compound $Ni_2Fe_3V_3O_{11}$. Primary BR pieces were crushed by laboratory jaw crusher and then were ground by a planetary ball mill. Grinding was continued until whole milled powder passed through 100 mesh sieve (i.e. < 150 μm). SEM micrograph of BA powder is shown in Fig. 1. The elemental weight ratio of V:Fe in BR was 8.2. Technical grade Fe_2O_3 −325 mesh was added to boiler ash to decrease V:Fe ratio to 4 that is recommended for ferrovanadium products according to ASTM A102. Aluminum powder with particle size of 45 μm was used as the reducing agent. Some aluminum might be lost due to evaporation or encapsulation in molten slag. For supplying sufficient aluminum, more than stoichiometric aluminum is needed and 5% and 15% extra aluminum were examined. Calcium oxide as flux forming agent was added as well and 0.65 and 1 M ratio of CaO/Al were tested. All ingredients were mixed well and each 15 g of mixed powder was compacted in cylindrical steel die with pressure of 150 kg/cm^2 and 30 mm diameter pellets were made. SHS reactor was a magnesia lined mill steel cylinder. Interior of reaction chamber had the height of 200 mm and diameter of 60 mm. Fig. 2 shows the refractory lined steel reactor for SHS process. In each test, 225 g BR was processed and every entire batch exceeded 400 g. These tests were designed to produce 115 g metallic master alloys with vanadium to iron ratio of 4:1. Pressed pellets were charged into the reactor and SHS reaction was started by ignition of a magnesium strip. Each SHS test tacked about 45 s. The microstructure of metallic specimens was studied by scanning electron microscope (SEM) and chemical composition of phases was measured by energy disperse spectroscopy (EDS).

The total efficiency of SHS was defined as Eq. (1):

$$E_t = \frac{\text{Weight of SHS product}}{115\text{ g (Theoretical yield)}} \times 100\%. \quad (1)$$

If vanadium and iron could be completely reduced, 115 g metallic product was produced in each test. Total efficiency demonstrates that how much metallic phase has been produced but cannot explain the contribution of each element. For clarifying the behavior of each element, elemental efficiency was defined as Eq. (2):

$$E_x = \frac{\text{Weight of element x in SHS product}}{\text{Weight of elemental x in 225 g BR}} \times 100\%. \quad (2)$$

x: V,Ni,Fe.

Elemental efficiency has shown how much of vanadium has been reduced and entered to metallic products as well as iron and nickel.

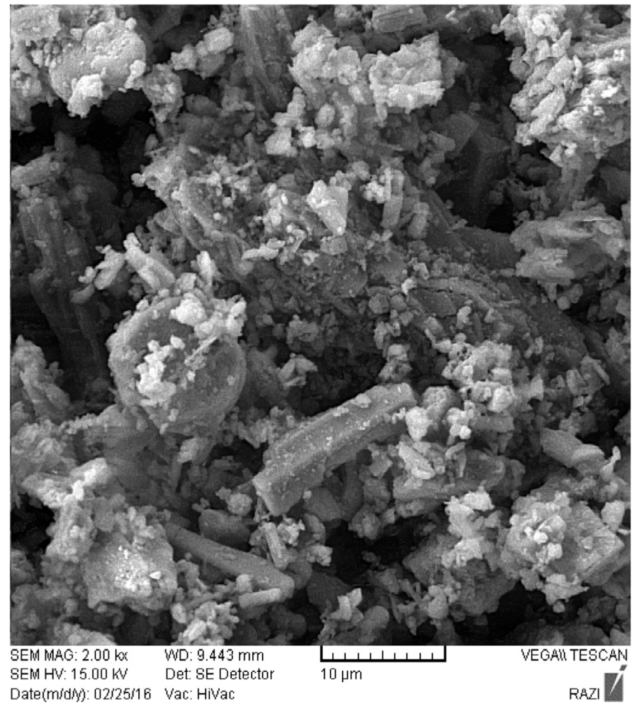

Fig. 1. SE-SEM micrograph of ground boiler ash powder.

Fig. 2. The magnesia-lined steel reactor for the SHS process.

3. Results and discussion

3.1. Total efficiency

The effect of extra aluminum supplementary to stoichiometric and Cao/Al ratio on SHS efficiency is illustrated in Fig. 3. The total efficiency of SHS tests was increased by increasing extra aluminum. Some aluminum is usually wasted in SHS tests by evaporating, oxidation or isolation from other ingredients (Yücel et al.,

Table 1
Total mass of each element in 100 g boiler residue calculated from XRF results.

Element	Na	Mg	Al	Si	S	Ca	K	V	Fe	Ni
Mass (g)	3.41	0.12	0.95	0.75	0.14	0.62	0.15	40.72	4.96	3.14

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