Optimization for leaching kinetics of vanadium pentoxide from thermal power plants fly ash using Taguchi approach

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Abstract

In order to reduce the environmental impact due to land disposal of heavy oil fly ash from thermal power plants and to valorize this waste material, recovery of vanadium was investigated using leaching processes (alkaline leaching). The recovery of vanadium has been adjusted via two stages. The first stage done was the thermal treatment process (burning process) at 650 and 850°C in order to reduce the carbonaceous fraction. The second stage established was the selection of sodium hydroxide for vanadium leaching. It was found to be the more selective for vanadium versus other transition metals is with addition of different percentage of sodium carbonate. Addition of sodium carbonate was found to be effective oxidant agent to increase the leaching efficiency. The optimal leaching solution was 80%vol. NaOH + 20%vol. Na_2CO_3. Taguchi design of experiments was applied to determine the optimum conditions for vanadium leaching. These are 4 M concentration, 2 h leaching time, 100:1 liquid to solid ratio.

Keywords: Vanadium; Heavy fuel; Fly ash; Leaching; Recovery.

1. INTRODUCTION

Fly ash is a solid residue generated during combustion of oil in the power generation station uses heavy oil [1].Fly ash contains one or more of the following elements in varying percentage such as Al, Ga, Ge, Ca, Cd, Fe, Hg, Mg, Na, Ni, Pb, Ra, Th, V and Zn. Among of these metals Ni and V is the most valuable [2]. Before disposal of fly ash into environment, it is important to extract the valuable elements such as V, Ni and other poison metals to reduce the harmful effect on the soil and water [3-5].

Vanadium is an important material that used in various fields such as the production of special steels, glass industry and to production temperature-resistant alloys [6-8]. Adding vanadium to ferrous and non-ferrous alloys can improve their physical, chemical and mechanical properties such as tensile strength, hardness, fatigue resistance, corrosion resistance and wear resistance [9, 10]. It considers as main strategic metal, therefore, renewed sources for vanadium production have to be established to face the continuous needs of vanadium. This is due rapid depletion of the vanadium ores [11]. For this reason, the recovery of vanadium from fly ash has received high attention in recent years and high priority. On the other hand, the disposal and accumulation of this industrial waste may lead to environmental problems. Several methods have been employed to recover Vanadium from fly and boiler ashes using hydrometallurgical processes. The leaching process may be carried out directly by acid solution [12-13], alkaline solution [14] or by water [15].

The aim of this work is to select the optimal modified alkali solution for leaching vanadium from fly ash. The effects of the main system variables on the leaching rate are examined by using Taguchi approach.

2. EXPERIMENTAL PROCEDURE

Heavy oil fly ashes select in this study is collected from AL-Hartha power station, Basra, Iraq. Mineralogical and chemical analyses of the fly ash are determined using scanning electron microscopy (SEM) and X-Ray fluorescence spectroscopy analysis. Energy dispersive spectroscopy equipped with SEM confirms the higher percentage of carbon (Fig. 1). This collected fly ash has porous nature of the particles (Fig. 2).The main chemical compositions of fly ash studied are listed in Table 1. Fly ash was crushed in a jaw crusher in the range of approximately 1 to 3 mm. The crushed fly ash was dried at 110 °C for 15 minutes. The grinding process carried out using ball milling machine for 15 minutes and 250 rpm and rotating speed. The final particle sizes of fly ash are in the range of less than 1000 µm

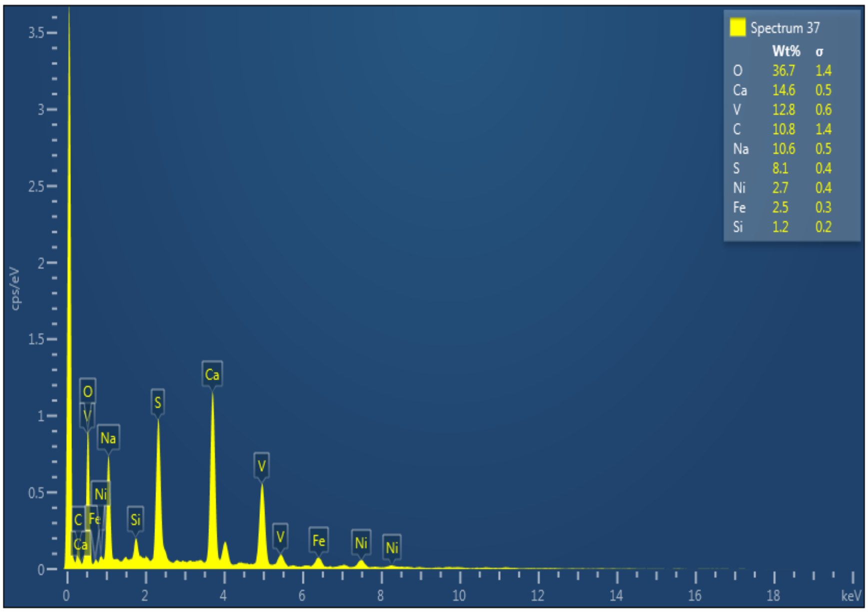

Fig. 1. EDS spectrum of heavy fuel petroleum fly ash.

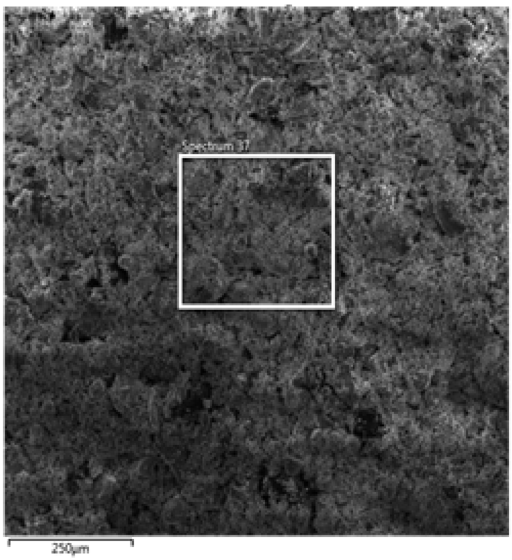

Fig. 2. Scanning electron microscopy (SEM) image for the fly ash investigated.

Table 1.chemical analysis of fly ash.

Element	V	Fe	Ni	Mg	S	Cr	C	Remain
Weight %	10.57	1.82	5.39	1.48	36.96	0.03	4.38	Co,Ca, Na, Al

Prior for sieving process, the fly ash was dried at 110°C. Different sieves in the sequence of + 1 mm, 1 mm, 500 µm, 250 µm, 212µm, 150 µm, 106µm, 75µm and 53 µm plus the pan were used. The agitation of the sieving system is taken place by mechanical means for 15 minutes. Fly ash retained in all sieving and the pan was weighted accurately. It is well known and accepted that the fly ash regardless the type of fuel used contains different compounds such as silica, calcium, alumina and other compounds. In this study, the effect of burning process of fly ash at temperatures of 650 and 850 oC were utilized.

Leaching experiments were carried out using 1000 ml glass reactor consists of round bottom three-neck flask. The purposes of these necks are to measure the temperature using thermometer, condensing and the third one for inlet fly ash. The setup of leaching reactor was placed on heater magnetic stirrer. The stirring speed was kept constant at 600 rpm. For each run 400 ml of leaching solution containing a determined concentration of leaching solution was charged into the glass reactor and heated to the 100°C. Once the leaching solution reached the desired temperature, specific weight of fly ash was added to the reactor and the leaching was carried out for a desired time. At the end of leaching time, the solution was filtered and analyzed to determine the metal ion concentration in the solution. It should be reported that the leaching efficiency has been calculate using the following equation [16]:

$$LE\% = [(((C.V)/(1000.P)))/(X/100)]100\% \quad (1)$$

where, LE is the leaching efficiency (%),C is the concentration of the metal in the solution (g/ml), V is the volume of the solution (ml), P is the mass of the solid sample (g) and X is the mass concentration of metal (%).

Different leaching alkaline aqueous solutions were used to select the best solution for higher leaching efficiency for vanadium. Four alkaline solutions based on

NaOH were investigated. Different volume percentages of sodium were mixed with NaOH solution. All experiments were carried at 100 °C at atmospheric pressure. It was found that the higher leaching vanadium recovery obtained by using solution of 80%vol NaOH+ 20% vol Na2CO3 as shows in Table 2.

Table 2. Leaching efficiency of vanadium at different leaching solutions.

Leaching solution	Leaching efficiency
NaOH	45%
20% NaOH + 80% Na_2CO_3	53%
50% NaOH + 50% Na_2CO_3	66%
80% NaOH +20% Na_2CO_3	81%

The experiments were designed by the use of Taguchi approach (Orthogonal Array). Taguchi orthogonal arrays □9(3^3) was established for experiments. The Taguchi design of experiments was done at three variables and three levels: leaching time, 2, 3.5 and 5 hr, concentration, 8, 4 and 12 M and liquid to solid ratio (L/S), 20/1, 60/1 and 100/1. Each experiment was repeated three times and the average was calculated.

Results and Discussion

Chemical analyses were made for all particle size to determine the amount of vanadium as shown in Table 3. Chemical analyses of the different particle sizes show that the presence of considerable amount of vanadium in all size of particles. Therefore, it was decided to use all the sieve powders for leaching process.

Table 3. The average wt.% of V for the fly ash leached.

sieve	Sieve name	Weight (g)	Weight (%)	Wt.% V	Fraction of V wt%
+1mm	1mm	0	0	0	0
-1+500	500	30.84	10.28	16.784	1.730
-500+250	250	41.86	13.95	12.708	1.731
-250+212	212	30.19	10.06	11.691	1.176
-212+150	150	30.78	10.26	10.271	1.054
-150+106	106	29.13	9.71	13.405	1.302
-106+75	75	29.26	9.75	12.357	1.205
-75+53	53	27.61	9.20	9.088	0.837
-53	Pan	69.23	23.07	8.731	2.014
Dust loss		11.1	3.7		11.048
Total		300	99.98		

reduction of carbonaceous fraction by thermal treatment. This allows more concentration of vanadium in fly ash to be present. The apparent contradictory results were achieved on leaching efficiency after burning process. The leaching efficiency decreased with increasing the burning

It was found that the concentrations of vanadium were increased considerably by a factor of approximately more than three times at 850 °C (Table 4). This means that the percentages of vanadium in fly ash increase with increasing the burning temperature. This is believed due to the vanadium concentration in the fly ash may due to the formation of less leachable vanadium compounds. temperature (Table 5). The reason for reduction of leaching efficiency with thermal testaments regardless the high

Table .4 Berning temperature on vanadium concentration of fly ash.

Burning temperature, °C	Vanadium before burning process, %	Vanadium after burning process, %
650	5.024	17.389
850		29.634

Table 5. burning temperature on leaching efficiency of vanadium.

Burning temperature, °C	%leaching efficiency unburned fly ash, %	%leaching efficiency burned fly ash, %
650	81%	73%
850		65%

The maximum scatter for the nine experiments is less than 2%. This repeatable and reproducible leaching reflects the high controllable experiments. The values of average leaching efficiency at different levels for the three variables studied are listed in Table 6. The corresponding efficiency of the three variables and their levels is described in Fig 3. It shows only the average efficiency of leach ability at different levels without any clear description of the effect of variables on the leaching efficiency.

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Table 6. Leaching efficiency of vanadium in solution of 80 vol.%NaOH + 20 vol.% Na_2CO_3.

Exp.	Time, h	Concentration M	L/S Ratio	Leaching 1, %	Leaching 2, %	Leaching 3,%	Average, %
1	2.0	4	20:1	91.498	93.142	91.773	92.138
2	2.0	8	60:1	98.231	97.105	97.524	97.620
3	2.0	12	100:1	64.199	64.035	66.961	65.065
4	3.5	4	60:1	96.851	96.545	95.913	96.436
5	3.5	8	100:1	78.818	79.004	78.981	78.935
6	3.5	12	20:1	21.487	21.571	20.957	21.338
7	5.0	4	100:1	85.969	84,968	86.540	85.826
8	5.0	8	20:1	30.086	30.605	31.207	30.633
9	5.0	12	60:1	47.279	47.093	44.996	46.456

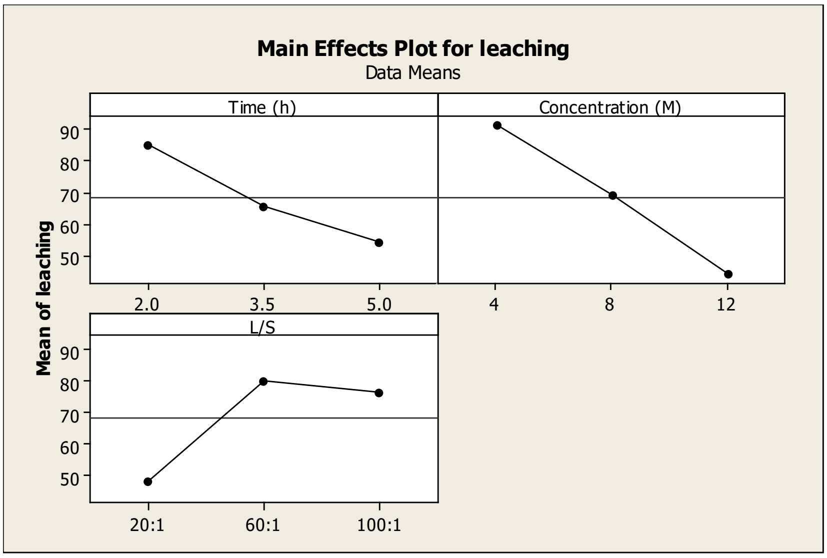

Fig. 3. Leaching efficiency for all variables at different levels.

The highest percentage recovery is required for many scientific and economic reasons in any recycling process. Since the goal of the leaching process is to achieve a highest degree of leaching efficiency of vanadium, therefore, for SNs ratio, a maximizing is needed for high quality. Table 7 lists the SN_Sfor all experiments and the related variables.Table 8 lists SN_S ratios for each level of the controlled factors. Fig. 4 shows the effect of controlled variables (factors) at different levels. The process performance for all variables at different levels and the rank for the variables with the values of delta are shown in Table 9. The contribution of each variable can be determined from the difference between the highest and lowest values of SNs for levels.

Table 7. The sequence of importance of variables controls the process.

Exp.	Time (h)	Concentration. (M)	L/S Ratio	Leaching 1 %	Leaching 2 %	Leaching 3 %	SNs Ratio
1	2.0	4	20:1	91.498	93.142	91.773	39.288
2	2.0	8	60:1	98.231	97.105	97.524	39.791
3	2.0	12	100:1	64.199	64.035	66.961	36.262
4	3.5	4	60:1	69.851	69.545	95.913	39.685
5	3.5	8	100:1	78.818	79.004	78.981	37.945
6	3.5	12	20:1	21.487	21.571	20.957	26.581
7	5.0	4	100:1	85.969	84,968	86.540	38.672
8	5.0	8	20:1	30.086	30.605	31.207	29.781
9	5.0	12	60:1	47.279	47.093	44.996	33.334

Table 8. Mean of SNs ratios of vanadium leaching for each variable at different levels.

Controlled factors	Average signal-to-noise ratio		
	Level 1	Level 2	Level 3
Time, h	38.447	34.737	33.909
Solution concentration, M	39.215	35.818	32.059
Liquid-to-solid ratio	31.863	37.603	37.803

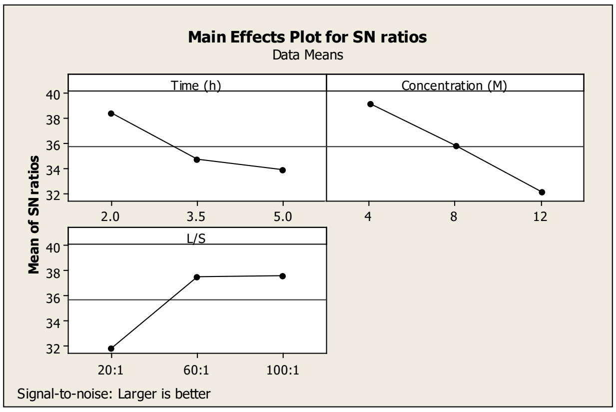

Fig. 4. SNs ratio on the efficiency of vanadium for all variables at different levels.

Table 9. Process performance and rank for each level at different variables.

Level	Signal-to-noise Ratio		
	Time, h	Concentration, M	L/S ratio
1	38.447	39.215	31.863
2	34.737	35.818	37.603
3	33.909	32.059	37.803
Delta, Δ	4.538	7.156	5.763
Rank of variables	3	1	2

percentages of contribution of each controlled factors to have effect on the leaching efficiency of vanadium from fly ash.

Table 10 lists the details of ANOVA and the resultant of it, where the variables are ranked in Table10are addressed with a value ρ% which determines the

Table 10. ANOVA of leaching vanadium for each controlled factors.

Controlled factors	DOFC	SS	MS	F Ratio	%ρ
Time, h	2	1479.7	739.8	13.37	21.916
Concentration, M	2	3343.9	1672.0	31.03	49.528
L/S Ratio	2	1889.6	922.8	17.54	27.987
Error	2	107.5	107.5	53.5	0.569
Total	8	6751.6	-	-	

According to the data of Taguchi design experiments, the solution concentration has the largest effect on the leaching process. It was found that the 4M concentration is the best for leaching vanadium to 97%. When decrease L/S ratio, the leaching efficiency increases. This may be due to the alkaline leaching agents. In general, alkaline leaching regents alone are considered as weak reagents in comparison with acidic leaching reagents. The time of leaching has the least influence on the leaching process among the three controlled factors. Leaching time curve shown in Figure 3explained that the reaction might be slow down as the time passes. This is because of consumption of the reactants. As the reactants concentration decreases, fewer collisions between vanadium molecules and H+ takes place. The influence of contact time is a function of temperature. Increasing the leaching temperaturemay lead to decrease the contact time require for soluble vanadium [17]. Therefore; according to the above points, leaching time of 2 hours seems to be sufficient in the leaching process.

4. Conclusion

1. The preliminary burning temperature of the fly ash in the range of 650 and 850°C allowed high concentration of the vanadium in the raw fly ash.
2. The burning process shows less leaching efficiency of vanadium from 81% to 73% and 65% at 650 oC and 850°C respectively.
3. Using alkaline solution of NaOH with 20 % vol. of sodium carbonate leads to high efficiency of leaching. It behaves as an effective oxidant agent lead to recover vanadium.
4. The solution concentration has the largest effect on the leaching process.
5. The efficiency of leaching is enhanced considerably with decreasing L/S ratio.
6. The time of leaching has the least influence on the leaching process among the three controlled factors.

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