Al-Nahrain University, College of Engineering Journal (NUCEJ) Vol.17 No.2, 2014 pp.197-202

Experimental Study on the Removal Process of Cobalt from Fly Ash using Different Solvents

Israa Shakir M. Ali
Collage of Engineering
Al-Nahrain University
E-mail: israa77shakir@yahoo.com

Abstract:-

In fly ash of thermal power plant, there are plenty of valuable metals, such as nickel, cobalt, iron. Recovery of valuable metals from fly ash not only protects the environment but also improves the utilization of resources. This study investigates the leaching process of cobalt from fly ash. A two-level three-factor full factorial design was successfully employed for experimental design and analysis of the results. The combined effects of type of solvent, concentration of solvent, time of stirring and temperature on the removal of cobalt were assessed using response surface methodology. The results showed that the maximum yield of cobalt 93% was obtained using 6 M hydrochloric acid as leaching solvent, at time of 68 min. and 45° C temperature.

Keywords:-Cobalt, hydrochloric acid, fly ash, time, temperature

Introduction:-

Disposal of a growing amount of waste from thermal power plant such as fly and bottom ash creates environmental problems due to the leachability of their heavy metals contents. However, fly ash is major components make it a potential agent for the adsorption of heavy metal contamination in water. It becomes more and more important to partly satisfy the world demand for metals through recovery of metals from secondary resources such as fly ash.

Many methods are applied for this purpose such as leaching with sulphuric acid (Pietrellii and Bellomo, 1999(1) and Li et.al., 2008(2)), mixed acid (Yanting et al., 2005)(3), electrolysis method (Lupi and Pasquali , 2003)(4).

Fruergaard,2013(5) stated that The leaching behavior of fly ash from a Co smelter situated in the Zambian Copper belt was studied as a function of pH (5–12) using the pH-static leaching test. Various experimental time intervals (48h and 168h) were evaluated. The largest amount of Co was leached at pH 5, generally with the lowest concentrations between pH 9 and 11 and slightly increased concentrations at pH 12.

Norris, et al., 2010(6) focused on determining the leachability of selected elements sequentially leached in four extraction solutions: water, 1M ammonium acetate, 3 M hydrochloric acid and 50% hydrofluoric acid. They evaluated the steps evolved in the leaching process with the mass recovery for each element being the basis for evaluation. The total amount of each element that leached out under the given extraction condition was presented as a fraction of the total present in the material. They evaluated NIST cool and fly ash standards. They measured different elements such as aluminum, calcium, cobalt, iron.

SanlIyuksel et.al., 2009(7), measured adsorptions of heavy metals using inductively coupled plasma atomic emission spectroscopy. They showed that the particle size and surface area of the ash are the most important factors affecting the extent of metal removal. They determined the adsorption capacity of fly ash as following: Cd>Cu>Cr>Pb>Zn>Ni>Co>Mn.

Evans et.al., 2010(8), they studied the use of South African coal fly ash, an industrial by product, has been investigated as a potential replacement for the current costly adsorbents use for removing heavy metals from wastewater. The adsorption was carried out in the presence of phenol and other heavy metal ions using the batch technique. The applicability of the Freundlich and Langmuir models to the equilibrium data was tested. Consequently, the equilibrium data was found to confarm more favourably to the Freundlichisotherm than Langmuir isotherm; in this study, the coal fly ash had a maximum adsorption capacity of 0.401 mg/g for cobalt (II).

Jinhui Liet.al.,2009(9), they used hydrochloric acid as lixivantfor the extraction of Ni, Co, Mn from spent battery material with characteristics of faster leaching rate and being recycled easily. The optimal conditions are that hydrochloric acid concentration is 6 mol./L, reaction time is exactly 60 C, (L/S) ratio is 8:1, $(H_2O_2)_{mol}/(MeS)_{mol.}=2$, leaching time is 2hr the results show that the dissolution yield of Co, Ni, Mn can be 95 wt.% at least.

Shang-Lin Tsai, Min-shing Tsai (1998)(10), they discussed the experimental extraction of vanadium and nickel from oil-fired fly ash. The results indicated that the leaching of oil-fired fly ash in 2 N sodium hydroxide solution, the extraction of nickel was negligible. If leached in an ammonia water, the extraction of nickel increased, along with an increase in the concentration of ammonia in water.

The aim of this study was to investigate the leaching conditions of cobalt from fly ash. The effects of type of solvent, concentration of solvent, extraction time, temperature on the yield of cobalt were studied using an experimental design technique.

Materials:-

Fly ash which was collected from (reheaters) of Al-Dora thermal power station in south of Baghdad, the composition of cobalt found to be (110 ppm). The composition found by atomic absorption spectrometry. Ammonium hydroxide NH_4OH was used as leaching agent, which is prepared from (25 %) NH_3.Also hydrochloric acid HCl was used as leaching agent, which is prepared from (35%) HCl.

Experimental Design:-

Central composite rotatable design (CCRD) was used to design the experiments and study the effect of three variables on the yield of cobalt. Surface response methodology was used to optimize the response surface and to determine the optimal conditions maximizing the cobalt yield. CCRD gives as much information as two –level factorial design but with a minimum number of experiments and also allows the user to analyze the interaction between parameters[4]. The solvent concentration (X_1), time (X_2), temperature (X_3) were the three parameters investigated in this work.

The range of selected variables was chosen based on preliminary experiments. The range of solvent concentration, time and temperature were (3-6 M), (15-120 min.) and (30-80 °C) respectively. The coded levels and the actual values of the three parameters for ammonium hydroxide solvent are shown in the following table:-

Design factor	-2	-1	0	+1	+2
X_1: NH_4OH (M)	3	3.5	4.5	5	6
X_2: time (min.)	15	40	68	95	120
X_3 : temperature (°C)	30	40	55	68	80

The coded levels and the actual values of the three parameters for hydrochloric acid solvent are shown in the following table:-

Design factor	-2	-1	0	+1	+2
X_1: HCl (M)	3	3.5	4.5	5	6
X_2: time (min.)	15	40	68	95	120
X_3 : temperature (°C)	30	37	45	55	60

The response factor (Y) was yield. The number of experiments required for CCRD was 20 with 2^k factorial points, 2k axial points and 2k replications at the center, where k is the number of factors [5].

Experimental Procedure:-

All cobalt leaching experiments were carried out in batch mode. 200 ml. beaker was loaded with solvent which was (NH_4OH) or (HCl) with a specified concentration (3-6) M, placed on a hot plate with magnetic stirrer. After reaching the desired temperature which was varied (30-80) ° C for ammonium hydroxide and (30-60) °C for hydrochloric acid, the ash was added with a solid to liquid ratio of (20g/100 ml.)[10] Which was the optimum ratio for the ammonium hydroxide solvent, or with a solid to liquid ratio of (5g/40 ml.)[9] Which was the optimum ratio for hydrochloric acid and then turning on the stirrer for mixing. After a specified time (15-120) min. of stirring. After leaching, the filtrate was determined for cobalt with the atomic absorption spectrometer

Results and Discussion:-

Table 1 leaching using ammonium hydroxide ($PPM_{initial}$=110)

Run No.	X_1, Concentration (M)	X_2, time (min.)	X_3, temperature (C)	Y, %cobalt leached
1	5	95	68	47.8
2	3.5	95	68	38.3
3	5	40	68	45.2
4	5	95	40	48.1
5	3.5	40	68	36
6	3.5	95	40	39.4
7	5	40	40	43.5
8	3.5	40	40	34.9
9	6	68	55	50.44
10	4.5	120	55	43.7
11	4.5	68	80	40.6
12	3	68	55	31.3
13	4.5	15	55	34
14	4.5	68	55	41.3
15	4.5	68	30	40.2
16	4.5	68	55	42.1
17	4.5	68	55	39.5
18	4.5	68	55	41.1
19	4.5	68	55	41.4
20	4.5	68	55	41.5

Table 1 shows the experimental values of the three variables and percentage yield of cobalt leached by NH_4OH solvent in each run. As can be seen, 31.3% of 110 ppm of cobalt was leached with 3M solvent at time of 68 min. and temperature of 55 °C. The percentage yield increased with increasing NH_4OH solvent concentration. It is clear that for the same concentration the yield increases with increasing in time until equilibrium reached. It also seen that the temperature has no effect on the yield.

That experimental plan enables to obtain the following second order polynomial model for percentage yield (Y) of cobalt leached (by ammonium hydroxide solvent) in coded values by applying multiple regression analysis:

$$y = 20.7966 + 0.86725X_1 + 0.15721\,X_2 - 0.1073\,X_3 + 0.00845\,X_1X_2 + 0.01488\,X_1X_3 - 0.001298\,X_2X_3 + 0.412599\,X_1^2 - 0.000344\,X_2^2 + 0.00126\,X_3^2 \quad \dots (1)$$

Coefficient of determination is high, R^2=0.9504, which means that the correlation is representative, because it clarifies 95.04% of all deviations.

The effect of different operating variables on leaching of cobalt by ammonium hydroxide (NH_4OH) is shown in 3-dimensional plots (figs.1, 2).

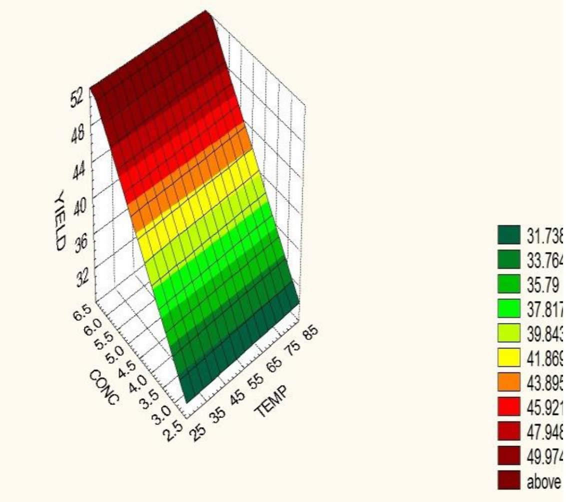

Figure (1): Response surface predictions of percentage cobalt leached by NH_4OH: effect of NH_4OH concentration and temperature.

Fig.1 showed the effect of ammonium hydroxide concentration and temperature on percentage yield of cobalt leached at a time of 68 min. the percentage yield of cobalt leached increases with increasing ammonium hydroxide at a fixed temperature. It is also observed that for a given value of ammonium hydroxide concentration, an increased in temperature dose has not significant effect on percentage yield.

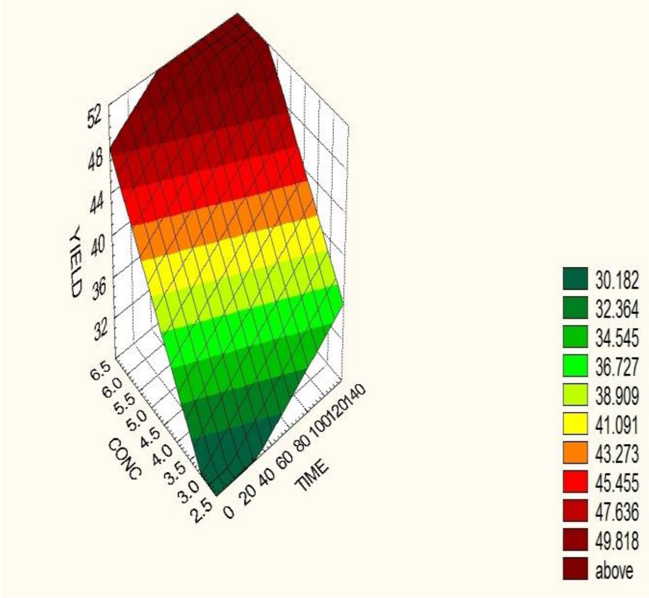

Figure (2: Response surface predictions of percentage cobalt leached by NH4OH: effect of NH4OH concentration and time of mixing

Fig.2 showed the effect of ammonium hydroxide concentration and time on percentage yield of cobalt leached at a temperature of 55 °C. The percentage yield of cobalt leached increases with increasing ammonium hydroxide concentration at a fixed time. It is also observed that percentage yield increases with increasing in time until the optimum value (95 min.).

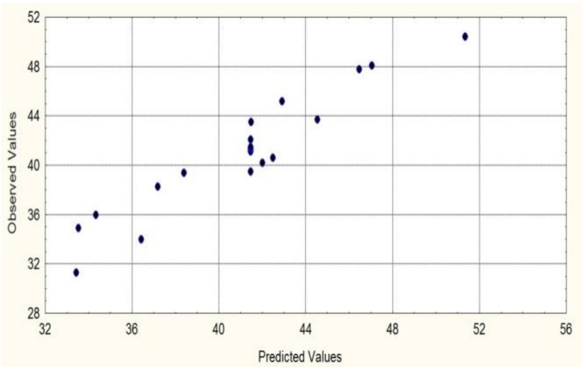

Figure (3): Comparison between the observed and the predicted percentage yield of cobalt leached by NH_4OH using the second order response model (equation 1).

Table 2 shows the experimental values of the three variables and percentage yield of cobalt leached by HCl solvent in each run. As can be seen, 86.3% of 110 PPM of cobalt was leached with 3M solvent at time of 68 min. and temperature of 45°C. The percentage yield increased with increasing in HCl solvent concentration, time and temperature, but temperature affects more than time.

Table 2: leaching using hydrochloric acid ($PPM_{initial}$=110)

Run No.	X_1, Concentration (M)	X_2, time (min.)	X_3, temperature (C)	Y, %cobalt leached
1	5	95	55	92.3
2	3.5	95	55	89.6
3	5	40	55	91.7
4	5	95	37	90.3
5	3.5	40	55	88
6	3.5	95	37	86.7
7	5	40	37	88.7
8	3.5	40	37	85
9	6	68	45	93
10	4.5	120	45	92
11	4.5	68	60	92.7
12	3	68	45	86.3
13	4.5	15	45	81
14	4.5	68	45	90.3
15	4.5	68	30	89.7
16	4.5	68	45	90.8
17	4.5	68	45	90.64
18	4.5	68	45	90.5
19	4.5	68	45	91.2
20	4.5	68	45	90.71

That experimental plan enables to obtain the following second order polynomial model for percentage yield (Y) of cobalt leached (by hydrochloric acid solvent) in coded values by applying multiple regression analysis:

$$\begin{aligned} Y &= 70.8419 + 1.9467\, X_1 + 0.004478\, X_2 \\ &- 0.271354\, X_3 + 0.087234\, X_1X_2 \\ &+ 0.73386\, X_1X_3 + 0.004314\, X_2X_3 \\ &- 0.01624 X_1X_2X_3 - 4.42157 X_1^2 - 0.001428\, X_2^2 \\ &+ 0.002967\, X_3^2 \qquad \ldots\ldots \quad (2) \end{aligned}$$

Coefficient of determination is high, R^2=0.9431, which means that the model is representative, because it clarifies 94.31% of all deviations.

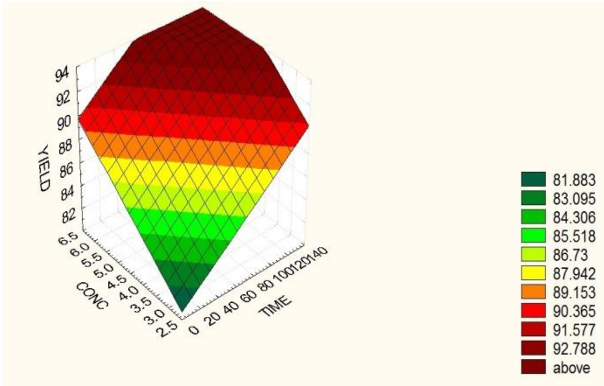

Figure (4): Response surface predictions of percentage cobalt leached by HCl : effect of HCl concentration and time of mixing

Fig.4 shows the effect of hydrochloric acid concentration and time on percentage yield of cobalt leached at a temperature of 45 °C. The percentage yield of cobalt leached increases with increasing hydrochloric acid concentration at a fixed time. Also the yield of cobalt leached increases with increasing time.

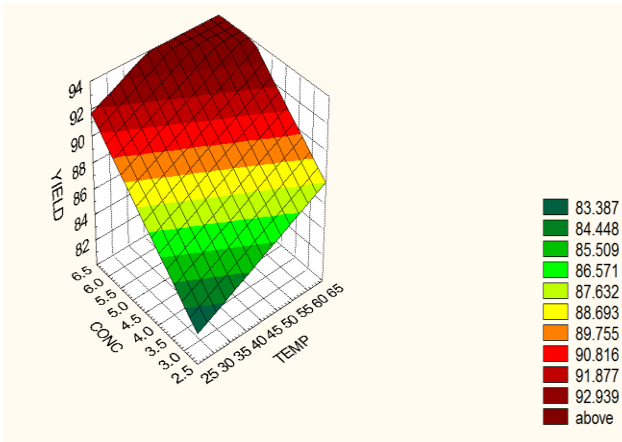

Figure (5): Response surface predictions of percentage cobalt leached by HCl : effect of HCl concentration and temperature

Fig.5 showed effects of acid concentration and temperature on the yield of cobalt leached at time of 68 min. The yield increases with increasing in the hydrochloric acid concentration at fixed temperature. Also increasing in temperature increasing the yield of cobalt leached.

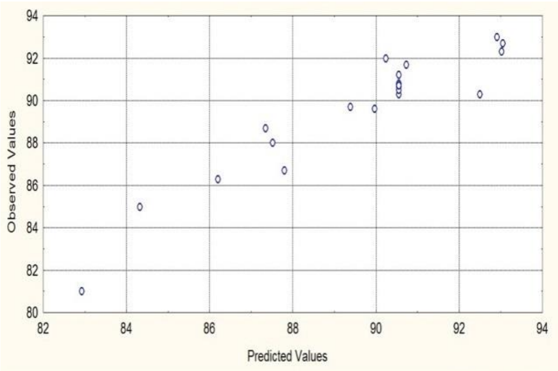

Figure (6): Comparison between the observed and the predicted percentage yield of cobalt leached by HCl using the second order response model (equation 2).

Conclusions:-

1- The hydrochloric acid gives results better than ammonium hydroxide.
2- The maximum yield of cobalt was found to be 93% using 6 M hydrochloric acid as leaching solvent, at time 68 min. and temperature 45 °C.

References:-

1- Pietrellii and Bellomo,L, 1-Pietrellii, B,Bellmo" Metal recovery from Ni-MH batteries: characterization and leaching tests", proceedings of the 5th international Battery Recycling Congress, France, Deauville, pp. 27-29, September, 1999.

2- Li Yunjiao, llyaPerederiy, Vladimiros G. Papangelakis" Cleaning of waste smelter slages and recovery of valuable metals by pressure oxidative leaching" Journal of Hazardous Materials, 152(2), pp. 607-615, 2008.

3- Yanting X., Yanbin X., Lan Y., Rudong Y." Recovery of nickel, copper and cobalt from low grade Ni-Cu sulfide tailings" Hydrometallurgy, 80, pp.54-58, 2005.

4- Lupi C., Pasquali M., “Electrolytic nickel recovery from lithium ion batteries" Minerals Engineering, 16, 6, pp. 537-542, 2003.

5- Astrup, Thomas Fruergaard, "Stability and leaching of cobalt smelter of fly ash", Applied Geochemistry, vol. 29, pp. 117-125, 2013.

6- Pauline Norris, et.al., "A technique for sequential leaching of coal and fly ash resulting in good recovery of trace elements", Science Direct-Analytica Chimica Acta, vol. 663, Issues 1, p. 39-42, march 2010.

7- Deniz Sanliyuksel, et al., " The adsorption of heavy metals onto waste from thermal power plant: A case study: Can thermal power plant, province of Canakkale, Turkey", World of coal ash conference, 4-7, 2009.

8- Evans T. Musapatika[I]; Maurice S. Onyango[II]; OchiengAoyi[III] "Cobalt (II) removal from synthetic wastewater by adsorption on South African coal fly ash", Academy of Science of South Africa, 2010.

9- Jinhui Li, Xinhai Li, et al.," Study of extraction and purification of Ni, Co and Mn from spent battery material" Science direct, Hydrometallurgy, vol.99, issues 1-2, Pages 7-12, 2009 .

10- Shang-Lin Tsai, Min-Shing Tsai, " A study of the extraction of Vanadium and nickel in oil-fired fly ash" Elsevier, resources, conservation and recycling, 22, 163-176, 1998.

11- Beltran-Heredia J, Sanchez- Martin J and Delgado A, Removal of dyes by Moringa Oleifera seed extract. Study through response surface methodology. J Chem Technol Bio Technol 84:1653-1659, 2009.

12- Box G and Draper N, Emperical Model Building and Response Surfaces. John Wiley and sons, New York, 1987.

دراســـة عمـــلية لعمـــلية ازالة الكوبـــلت من الرمــاد المتطــاير بإستخــدام مذيبــات مختلــفة

م.م. إسراء شاكر محمد علي
قسم الهندسة الكيمياوية - جامعة النهرين

الخلاصة:-

يحتوي الرماد المتطاير من محطات الطاقة الحرارية على الكثير من المعادن الثمينة مثل النيكل، الكوبلت والحديد. استرداد هذه المعادن لايحمي البيئة فقط وانما يوفر مصدر لهذه المعادن. هذه الدراسة تبحث في عملية استخلاص الكوبلت من الرماد المتطاير بأستخدام طريقة رياضية للتصميم العملي وتحليل النتائج. تم دراسة تأثير نوع المذيب، تركيز المذيب, وقت الخلط والحرارة على ازالة الكوبلت بطريقة الاستجابة السطحية. اظهرت النتائج ان اعلى نسبة للكوبلت 93% تم استحصالها بأستخدام 6 مولاري حامض الهيدروكلوريك كمذيب بزمن 68 دقيقة ودرجة حرارة 45°م.