Preliminary Study on the Regeneration of Spent Electro-decontamination Solution Using Phosphoric Acid and Oxalic Acid

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1. Abstract

In this study, different amount of (fe(0)) were dissolve into different strength of phosphoric (H_3PO_4) acid and the optimum solubility was observed at 0.89M Fe(0) into 4M of H_3PO_4 acid. Different concentration of oxalic acid was added to determine the optimum precipitated condition. The dissolution kinetics of Fe(0) into H_3PO_4 acid was investigated at 40-50°C . The optimum Fe-oxalate precipitate was dried and thermal decomposition using DSC-TG was conducted. Approximately 52 wt(%) of oxalic acid was removed at 300°C. Iron oxides such as magnetite and hematite that may be formed on the surface of nuclear waste were also dissolved into the H_3PO_4 acid and the optimum solubility for magnetite is 0.005M while that for hematite is 0.02M in 8M H_3PO_4 acid, respectively.

2. Introduction

In Korea, some nuclear power plants have been operating for more than 3 decades. Electrochemical decontamination may be considered in principle to be the chemical decontamination assisted by an electrical field. It may be considered as the opposite of electroplating since metal layers are removed from a surface rather than added as a coating. This experiment suggests a procedure capable to improve the control of the decontamination process to be applied in a power plant, attempting to predict and optimize treatment time in order to improve the efficiency of the plant and minimize the produced wastes (mainly Fe and other metals including Ni, Co, Cr, etc.) as the most cost-effective and quick process of waste removal by using phosphoric acid and other organic acids. Phosphoric acid is very efficient for removing radioactive contaminants and providing a smooth surface.

3. Materials and Method

Iron (Fe(0), purity: min. 98%), oxalic acid ($C_2H_2O_4.2H_2O$, purity: 99.5~100.2%), hematite (Fe_2O_3, purity: min 95%) were purchased from Kanto chemical Co. Japan, magnetite (Fe_3O_4, purity: above 95%) from Daejung Chemical & Metal Co. Korea, phosphoric acid (H_3PO_4, purity: above 85%) was purchased from Merck, Germany. Different concentration of H_3PO_4 acid (1M, 2M, 4M, 6M and 8M) has been prepared and then different amount of Fe(0) was dissolved into each H_3PO_4 acid concentration using Teflon stirrer at 200 rpm for 3.5 to 12 hr. at (25, 40, 50, 60, 70°C) to obtain optimum solubility. Oxalic acid of different concentration (0.5M, 1M, 1.5M, 2M, 2.5M, 3M, and 3.5M) has been added to the optimum Fe solution to have best precipitation. Total Fe content measured by ICP-OES, OPTIMA 2100DV, Perkin Elmer), DSC-TG (Differential Scanning Calorimetry- Thermogravimetry) analysis of Fe-oxalate has been done by using SDT Q600 (TA Instruments, UK). Magnetite and hematite were prepared (0.2M, 0.09M, 0.02M, 0.009M, and 0.005M) and dissolved to 4M and 8M H_3PO_4.

4. Results and Discussion

Table 1. Optimum solubility of Fe(0) into H_3PO_4 acid

H_3PO_4 (M)	Fe (M)	T(^{o}C)	Reaction time (hr)	Dissolution	Image
4	0.89	40	5	no	
		50	3.5	yes	
	1	25	12	no	
	1.5	25	12	no	
	2	25	12	no	

Table 1. shows the solubility of Fe (several concentrations) observed into 4M H_3PO_4 acid and it is investigated that 0.89M of Fe dissolve into the 4M H_3PO_4 acid at 50°C finely.
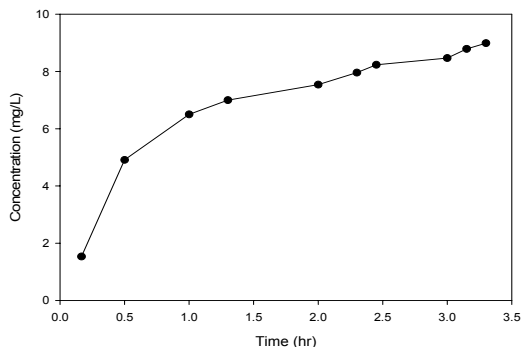

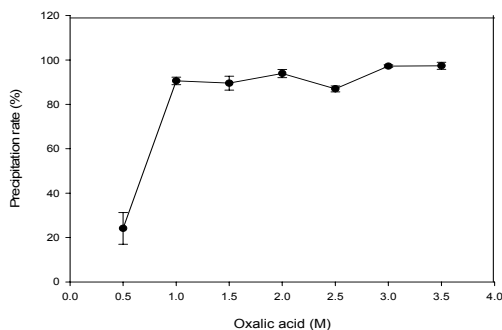Fig. 1. Dissolution kinetics of Fe(0) into H_3PO_4 acid.

Fig. 2. Precipitation of Fe(II)-oxalate.

Fig.1 shows the dissolution kinetics of 0.89M of Fe into 4M H_3PO_4 acid at 50°C within 3.4 hour and Fig. 2. depicts the precipitation rate of Fe-oxalate at different concentration of oxalic acid and high precipitation rate has been observed for 1M to 3.5M of oxalic acid.
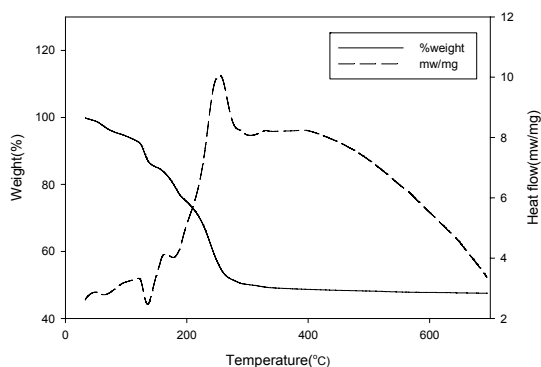

Fig. 3. DSC-TG of Fe-oxalate in air.

In Fig. 3 The TG (Thermogravimetric) curve of Fe-oxalate powder can be divided into few temperature interval and weight loss 4.466% at 75-100°C, 24.5% at 200°C and approximately 52% at 300°C. The total

weight loss at 500 does not correspond to the formation of the expected compounds (Fe, FeO, Fe_2O_3, and Fe_3O_4) as a single phase. The DSC (Differential Scanning Calorimetry) curve shows a narrow endothermic effect at 125-150°C and a broad exothermic peak over the range from 200-300°C accompanied by TG curve showing the weight loss of 27.27%.

Table 2. Optimum solubility of Magnetite and Hematite

H_3PO_4 (M)	Magnetite(M)	T(°C)	Reaction time (hr)	Dissolution	Image
8	0.005	50 to 60	2	yes	
	Hematite (M)				
4	0.02	40 to 50	4	yes	
8		40 to 50	4	yes	

Table 2 shows that magnetite dissolve to 8M H_3PO_4 acid of at its 0.005M at 50 to 60°C temperature range whereas 0.02M hematite dissolve at 4M and 8M H_3PO_4 acid at same temperature range

5. Conclusion

Fe(0) powder has been dissolved to 4M H_3PO_4 acid at 50°C and 1M oxalic acid has been considered as the optimum condition of precipitation with Fe-oxalate. Later, on decomposition oxalic acid removed at high temperature(at 300°C the weight loss is 52% approximately). Optimum solubility for magnetite and hematite found at 0.005M and 0.02M respectively into 8M H_3PO_4 acid.

6. References

[1] T. Izumida, K. Kato, F. Kawamura, H. Yusa,"Electrolytic deontamination of surface-contaminated metal by alternating electrolysis using square-wave current in a neutral salt electrolyte", Radioactive Waste management, 70, 249-253 (1985).

[2] M. Harmanek, R. Zboril, M. Mashlan, L. Machala, O. Schneeweiss, "Thermal Behavior of Iron (II) oxalate Dihydrate in the Atmosphere of its Conversion Gases", Journal of Materials Chemistry, 16,1273-1280 (2006).