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Stabilization of Effluent Treatment Plants Generated Nickel Sludge by Thermo-Chemical Treatment

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Metal finishing industries, in their effluent treatment plants (ETP) produce sludge containing heavy metals. These are categorized as toxic solid wastes and hence need special disposal. In the present work experimental studies have been conducted on Ni-bearing ETP sludge to find out the feasibility of stabilization/fixation by thermochemical treatments to non-leachable detoxified form so that when disposed on land, there should be no leachability of nickel either to the soil matrix or seepage to ground water.

Key Words: Effluent treatment plants, Nickel-sludge, Fe (pickling sludge), Thermo-chemical treatment, Stabilization/Fixation, Leaching.

INTRODUCTION

Electroplating and metal finishing industries generate sludge containing heavy metals. Though the metals are precipitated as their hydroxides, carbonates or sulphides (insoluble forms), still potential for leaching of the heavy metals from the sludge do exist[1]. These wastes contaminate the nearby flowing water bodies through lateral migration of leachate and surface run of pollutants[2]. Due to high toxicity and their adverse effect on human beings, animals and plants[3, 4], treatment and detoxification of these wastes poses a great challenge to the scientists and environmentalists.

Understanding the mechanism that influences heavy metal manufacturing operations or waste treatment methods and mobility are important. Because this will determine the methods most suitable for stabilization/fixation (S/F). The primary objective in employing S/F technique is to minimize the mobility of metals by reducing their dissolution in natural environment. This should be done in a manner that inhibits the contamination of ground water. A waste stream must be solidified before being land disposed. Solidification involves addition of materials like lime, fly ash, cement, etc. But these do not stop leaching. Basically, the stabilization process is an encapsulation (or bonding) process involving the reaction between residual water present in the waste and chemical additive or

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binder. The process of fixation converts the waste into a chemically fixed, easily transportable solid. The binder acts with the hazardous constituent to form a chemically altered new compound which has become non-toxic through physical immobilization and chemical alteration, which is rendered non-leachable. According to RCRA (Resource Conservation Recovery Act legislation of 1976)[5], the code of the waste, which has been attempted for stabilization is F006 (waste water sludge from electroplating industries). Chemical waste management (CWM) has conducted laboratory studies on stabilization of F006 sludges.

The chemical additives are termed as binders. As defined by US Environmental Protection Agency (USEPA) stabilization using binders is the best demonstrated available technology (BDAT) under the title 40 parts 268 of the code of the Federal Regulations (40 CFR 268).

Binders could be inorganic or organic[7, 8] in nature. Urea formaldehyde polymerisation monomers, polysulphide/epoxy systems, chloromethylated polystyrene[9], chelating resins[10] have been used as organic binders for heavy metals. Currently bitumen, asphalt, paraffin, high temperature polyethylene (thermoplastic agent), polyester residues, molten glass are also used as organic binders in many cases. For S/F process, common inorganic binders used are lime, cement, fly ash, pozzolan base agents, soluble silicates and mixed kiln dusts. Organic binders being expensive are used only for specific reactions, whereas inorganic binders find wide application. The chemically altered new compounds prior to disposal have been subjected to EPT or toxic characteristic leaching procedure (TCLP) test. For conducting such leaching studies USEPA has funded extensive studies to US Army Engineer Waterways Experiment Station (WES) to test the technique for variety of industrial wastes[11].

The metals, which are normally used for electroplating, are chromium, nickel, cadmium, zinc and copper etc. Of these, we have chosen Ni-sludge as the starting material for this study. Nickel recovery from electroplating sludges has been attempted by many workers[12, 13]. Literature also reveals that lime[14–16]/calcium carbonate[17] has been used as binders for nickel containing sludge. Cement has been reported to be used as binder[18, 19] for stabilization/immobilization of heavy metals. Natural zeolite has also been reported to be used for stabilization of Ni-wastes[20]. Melting and subsequent solidification[21] has also been applied for immobilization of Cr, Cu, Ni, Pb, As and Zn. These stabilized wastes were subjected to TCLP and solid threshold leachate concentration (STLC)[22] tests. Detoxification of fly ash containing heavy metals[23] has been reported by removal of heavy metals through solidification and leaching studies. Literature review has shown that Fe salts have been used for immobilization of heavy metals[24, 25]. High temperature reaction of iron with nickel converts the latter into ferrite type compounds as seen in literature[26]. Also it has been shown[27] that by thermal treatment (at 1000°C) of Ni-sludge with Fe containing wastes at a fixed ratio stabilizes both the metals. Taking these as guidelines, an attempt was made to indirectly detoxify the sludge containing nickel by stabilization/fixation and leaching studies.

A process requiring 1000°C becomes energy intensive. So attempts were made to reduce the reaction temperature using different additives, so that the final compound could be made non-leachable for safe and environment-friendly disposal. Attempts were made to analyze the stabilized products by X-ray and other physical means to find similarity with any existing compound. Also disposal of the stabilized waste in a powder form might cause other environmental problems by flying across causing fugitive emission in the surrounding areas. Hence, it was also attempted to palletize the material and study its physical shape after thermal treatment.

The present work is an attempt to stabilize/fix the nickel sludge of an ETP through thermochemical treatment using various additives by experimental studies and indirectly to detoxify the sludge by leaching studies for safe and environment-friendly disposal of the same. Experiments were conducted in the laboratory so as to set the conditions for S/F and determine the metal dissolution through leaching studies.

EXPERIMENTAL

The sludge was collected from the ETP of a local electroplating industry, which uses only Ni-plating. Fe-sludge was collected from a pickling industry. All chemicals were purchased from E. Merck (India). Hot air oven, muffle furnace, pH-meter with combined glass electrode (procured from Elico, India) with temperature compensation (0–100°C) and calibrated at 30°C and spectrophotometer were used.

For physical characterization of the sample (after thermochemical treatment) magnetic moment, EDAX analysis and powder pattern X-ray using CuK_α radiation was performed. Also the samples pelletized using a press (AMIL-make with 5 ton load for 1 cm pellet).

In the present case, the sludge was mixed with water and the pH was observed to be 6. So to this sludge Na_2CO_3 was added and towards the end Na_2S (0.2 g/100 mL) was added and stirred. The resulting solution was checked for pH till it attained a pH of 8.5. The sludge, so produced, is termed as the standard sludge. The sludge was dried, powdered and sieved. The particle size used for the entire study was 0.710 mm. Iron sludge from the pickling industry was collected, dried in an oven, finely ground and sieved to the same particle size. For preparation of the mixture of Ni and Fe sludge (the binary mixture) both powders were intimately physically mixed using mortar and pestle.

Leaching studies

Following the procedure of USEPA[28], leaching studies were conducted with water and 0.04 m acetic acid at pH 5. It has been observed that metal solubility increases with increase in salt concentration. Hence, it was decided to study the leaching behaviour in salt solutions as well. In order to study the leaching characteristics of the materials in shorter time (1 h), a quick leaching process was developed in the laboratory. A number of experiments were conducted to test the validity of the method, termed as reflux leaching process (RLP). Some of the results of such a study conducted on Pb-containing wastes have been reported[29]. The RLP method was conducted keeping the solid : liquid ratio as 1 : 100, which was refluxed for 1 h, the liquid being water, 0.04 m acetic acid (pH 5) or salt solution [RLP_w, RLP_a and RLP_s respectively]. Leachability of the metal in the filtrate has been reported.

Standard sludge was thermally treated at 1000°C. Leaching studies were conducted both on the standard sludge as well as on the thermally treated sample. Both time and temperature were varied to study the effect on leaching. With the standard sludge Fe waste (dried) was added and physically mixed in different ratios. The binary mixture was thermally treated at 1000°C and leaching studies were conducted. As in the previous case, both time and temperature were varied to check the effect on leachability. Certain additives like fly ash, rice husk and lime etc. were added and subsequently leaching studies were conducted. The effect of additives on the binary mixture was also studied.

Metal ion analysis in the leachates was conducted spectrophotometrically at 510 and 445 nm for Fe and Ni respectively. At times metal ion concentrations were very low which could not be analyzed. These readings have been expressed as below detectable limits (BDL).

After establishing the non-leachable sample, physical measurements were conducted by sintering the material at 1150°C, since it melted at 1250°C. Magnetic moment of the non-leachable binary mixture was determined using EG&G Princeton Applied Research Vibration Sample Magnetometer (Model 155). The stoichiometric analysis of the elements present in the sample was conducted by energy dispersive analysis of X-ray (EDAX) using model ISIS 1000 & SEM Model. The structural analysis was done using Philips Diffractometer (Model PW 3020) using CuK_α (1.54 Å) radiation.

RESULTS AND DISCUSSION

Leaching tests were indicative of metal ion concentrations. So leaching studies were conducted on the untreated sludge (standard sludge). The results (Table-1) showed that metal concentration in the leachates is much higher than the permissible limit.

TABLE-1
LEACHING CHARACTERISTICS OF THE STANDARD SLUDGE (UNTREATED)

S.No.	Medium of leaching	Concentration of Ni (ppm)
1.	RLP w	22.5
2.	RLP a (0.04 AcOH)*	2300
3.	RLP s (0.005%)	3
4.	RLP s (0.1%)	35
5.	RLP s (1.0%)	37
6.	RLP (10.0%)	40

w: water, a: acid, s: salt

*Only acetic acid buffer was chosen, since the leachability is highest in this.

After thermally treating the standard sludge at 1000°C leaching studies were conducted and results have been shown in Table-2. Thermal treatment reduced the leachability in water and salt solutions; however it still remained very high with acid.

TABLE-2
LEACHING CHARACTERISTICS OF THE STANDARD SLUDGE AFTER THERMAL TREATMENT AT 1000°C

S.No	Leaching medium	Concentration of Ni (ppm)
1.	RPL w	BDL*
2.	RPL a	25
3.	RPL s (1%)	BDL*

*BDL = Below Detectable Limit.

Binary mixtures of the standard sludge were prepared with Fe in varying weight ratios of Fe while keeping Ni weight constant and the mixtures were thermally treated at 1000°C before leaching studies were undertaken. The results of leaching of both metals have been given in Table-3. At a weight ratio of 1 : 5 of Ni : Fe the metal concentration showed the minimum value, showing Ni at 1 ppm and Fe going to BDL. So this ratio of Ni : Fe (1 : 5) was chosen for the entire experimental study. Time and temperature were varied during the thermal treatment of this sample (Figs. 1 and 2).

It was observed that by increasing the thermal treatment time the metal ion concentration decreased to the minimum and 1 h was required to bring the metal concentration to the lowest value, after which the values remained constant

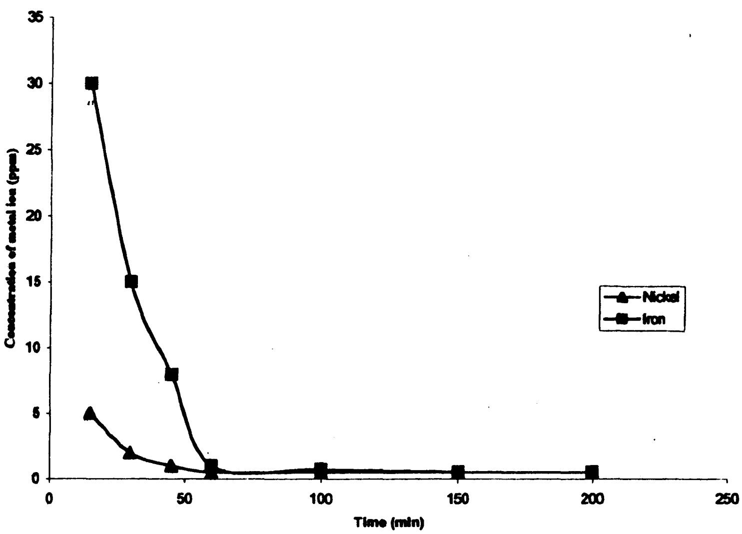

Fig. 1. Effect of time on the leaching characteristics of the binary system Ni : Fe (1 : 5) (Temperature 1000°C)

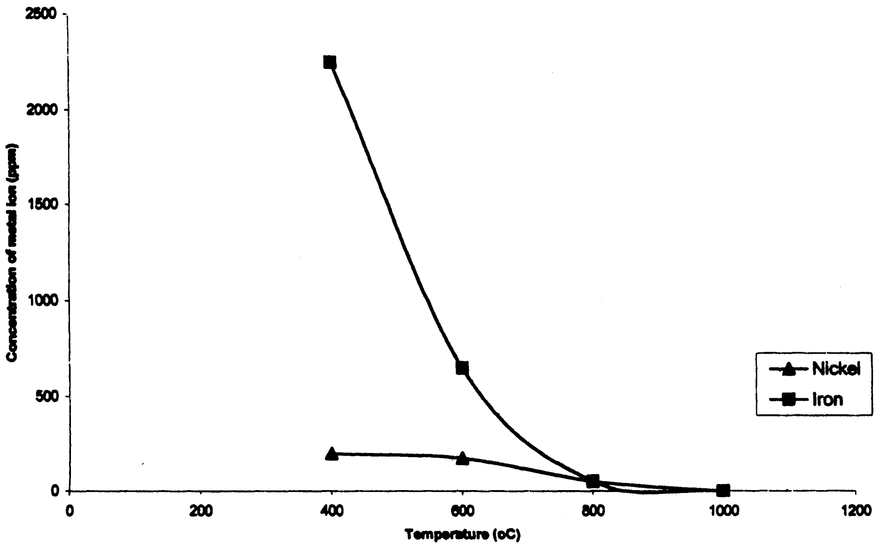

Fig. 2. Effect of temperature on the leaching characteristics of the binary system Ni : Fe (1 : 5)

(Fig. 1). Increase in the temperature of treatment, though had a profound effect on leachability was the minimum at 1000°C (Fig. 2 and Tables 3 and 4).

TABLE-3
LEACHING BEHAVIOR OF THERMALLY TREATED (1000°C BINARY MIXTURE OF Ni-Fe IN 0.04 M ACETIC ACID (BUFFER)

S.No.	Binary mixture (wt. ratio of Ni-Fe)	Metal concentration (ppm)	
		Ni	Fe
1.	1 : 1	5.0	2.0
2.	1 : 2	4.0	1.5
3.	1 : 3	3.4	1.0
4.	1 : 4	1.8	BDL
5.	1 : 5	1.0	BDL

TABLE-4
EFFECT OF TEMPERATURE VARIATION ON LEACHABILITY OF THE BINARY MIXTURE [Ni : Fe (1 : 5)]

S.No.	Treatment Temperature (°C)	Leachability (in ppm)
1.	400	2280
2.	600	785
3.	800	21
4.	1000	1

Since the binary mixture did not have any energy-giving component, different additives were tried so as to lower the temperature of reaction. Additives like lime, rice husk, fly ash and borax were attempted. Additions of lime/borax were done for possible reduction of reaction temperature. Rice husk and fly ash were added for supplementing partial energy needs of the process. Rice husk was chosen because of its abundant availability and being a cheap source of energy. Fly ash, generated from coal combustion creating environmental problem, is often used as aggregates for construction works. There remain some unburnt carbon, which can supply partly the energy needs of the process. The purpose of adding fly ash could have a possibility of the disposal of the detoxified metal as part of manufactured aggregate for building material. Ni-leachability was studied (because Fe leachability could be brought below detectable limit (Table-3). As observed in Table-5 it was evident that the leachability of Ni could also be brought down to BDL. So this method of treatment for S/F was accepted. It was also observed that using borax, the material could be compacted (pelletized) and after thermal treatment retained its shape. Compaction reduced the volume and disposal in compacted form had the additional advantage of avoiding any fugitive emissions from disposal site (in the form of fine dust), as has already been mentioned.

TABLE-5
WEIGHT RATIOS OF BINARY MIXTURES TO DIFFERENT ADDITIVES FOR THERMAL TREATMENT AT 800°C

S.No.	Binary mixtures : Additives	Ratio	Ni (ppm)
1. (a)	Binary mixture : Lime	1 : 0.0	21.0
(b)		1 : 0.1	8.4
(c)		1 : 0.2	10.5
(d)		1 : 0.5	12.5
2.	Binary mixture : Rice husk Lime	1 : 0.06 : 0.01	7.2
3. (a)	Binary mixture : Fly ash	1 : 0.3	2.0
(b)	Binary mixture : Fly ash : Borax	1 : 0.33 : 0.33	BDL

The stabilized compound was further analyzed through some physical measurements (Table-6) to establish any resemblance with any known compound specifically to ferrites as has already been mentioned[26, 27]. These physical measurements pointed out some resemblance to Ni- ferrite compound. So powder

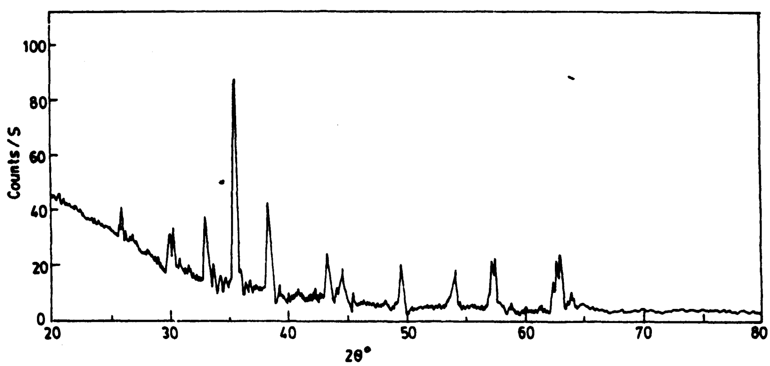

Fig. 3. X-ray analysis of thermally treated binary mixture

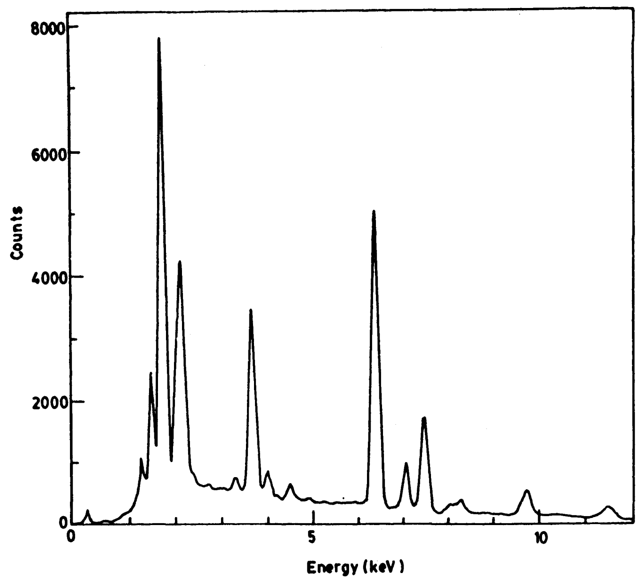

Fig. 4. EDAX analysis of thermally treated binary mixture

pattern X-ray of standard sludge (Table-7, Fig. 5) and that of the thermally treated binary mixture (Table-8, Fig. 3) were conducted. The d-spacing values were compared with standard Ni-ferrite as available (Table-9). They showed closer resemblance with the thermally treated binary mix of [Ni-Fe (1 : 5)] indicating that the binary mixture [ref. 2 (b), Table-5] is partially converted to Ni-ferrite type compound in addition to some other phases. In case of thermally treated standard sludge only two d-spacings with 5.93 and 5.82% relative intensity matched, whereas in the case of thermally treated binary mixture 10 values matched with % relative intensities being 37.3, 100.0, 5.36, 11.13, 17.25, 22.87, 3.92 and 4.65. This clearly indicated that a large part of the binary mixture was converted to ferrite type compound in addition to the presence of the other phases. EDAX analysis was done to find the stoichiometric metal concentrations as given in Fig. 4 and Table-10. The stabilized palletized sample (treated at 800°C) was tested for leachability (Table-5).

TABLE-6
PHYSICAL CHARACTERISTICS OF SAMPLE 3 (B) OF TABLE-5 COMPARED WITH Ni-Fe

S.No.	Tests	Non-leachable binary mixture	Ni-Fe
1.	Bulk density	2.74 g/mL	4.5–4.7 g/mL
2.	Magnetic moment	266 gauss	3000–3200 gauss
3.	Melting point	1250°C	—
4.	Sintering temp	1150°C	1250°C

TABLE-7
X-RAY ANALYSIS OF STANDARD SLUDGE

d-spacing (Å)	Relative intensity (%)	Angle 2θ (°)
4.18300	100.00	21.22260
3.91910	35.80	22.67002
3.78507	29.39	23.48400
3.46881	9.50	25.65995
3.08165	34.49	28.94991
2.81824	56.43	31.72376
2.64229	36.67	33.89800
2.46141	73.34	36.47336
2.26647	15.92	39.73656
1.97138	5.93	45.99992
1.72155	22.65	53.15822
1.56492	8.92	58.97264
1.45822	6.08	63.77233
1.32016	5.82	71.39085

TABLE-8
X-RAY ANALYSIS OF SAMPLE 3 (b) OF TABLE-5

d-Spacing (Å)	Relative intensity (%)	Angle 2θ (°)
4.25374	14.07	20.86570
4.03626	7.123	22.00360
3.34412	68.36	26.63400
3.19342	11.76	27.91571
2.98956	37.31	29.86216
2.94840	42.55	30.36866
2.50950	100.00	35.75047
2.45710	13.79	36.53955
2.29601	5.36	39.20429
2.12393	11.29	42.41527
2.07740	19.78	43.52878
2.02514	7.26	44.71180
1.81800	11.13	50.13639
1.69522	8.85	54.05063
1.59988	17.25	57.56176
1.47160	22.87	63.12519
1.37714	3.92	68.01925
1.08241	4.65	90.73595

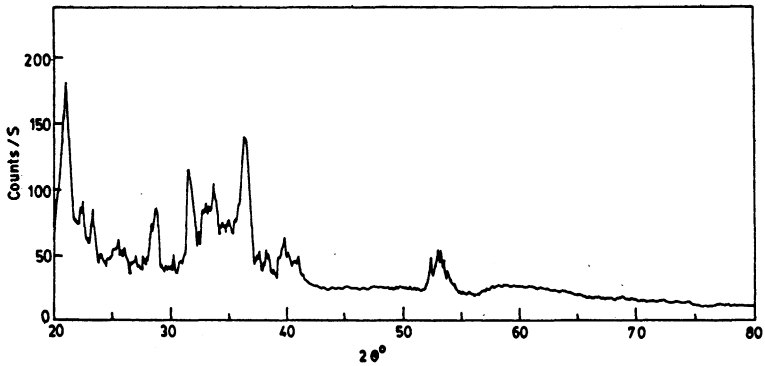

Fig. 5. Standard sludge X-ray

TABLE-9
X-RAY ANALYSIS OF NICKEL FERRITE (NICKEL IRON OXIDE, $NiFe_2O_4$) STANDARD DATA (30)

d-Spacing (Å)	Relative intensity (%)	Angle 2θ (°)
4.8200	20	18.3906
2.9480	30	30.4844
2.5130	100	35.6969
2.4080	8	37.3019
2.0850	25	43.3572
1.9125	4	47.5066
1.7025	8	53.7955
1.6051	30	57.3577
1.4760	40	62.9061
1.4100	2	66.2270
1.3187	6	71.4788
1.2706	10	74.6304
1.2573	4	75.5554
1.2036	6	79.5870
1.1676	< 1	82.5539
1.1145	6	87.4344
1.0857	16	90.3722
1.0424	6	95.2755
0.9827	2	103.2197
0.9630	10	103.4229
0.9566	2	107.2591
0.9324	8	111.4003
0.9152	2	114.6189

TABLE-10
EDAX ANALYSIS OF SAMPLE 3 (b) OF TABLE-5

Element	Atomic %	Element	Atomic %
Mg	5.17	Ca	11.23
Al	8.91	Ti	0.93
Si	35.22	Fe	32.34
K	1.05	Ni	5.15

*3 peaks possibly omitted 0.06, 9.70, 11.48 keV.

Conclusions

The stabilized form of the waste could be brought to a benign, non-leachable form through the formation of Ni-Ferrite with addition of Fe by thermal treatment. As aimed through the study, nickel sludge generated in effluent treatment plant could be made non-leachable.

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