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ANALYSIS PURIFICATION AND UTILIZATION OF WASTE FROM THE PAKISTAN - AMERICAN FERTILIZER INDUSTRY AT DAUD KHEL

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The utilization of solid industrial wastes greatly helps in reducing energy consumption which is to be required in shifting the waste to some disposable sites, in saving land and controlling pollution. Studies have been carried out to assess the chemical composition and into methods for the purification of the waste from the Pakistan-American Fertilizer (PAF) Industry. Results of chemical, sieve, thermogravimetric and differential thermal analysis have been presented and discussed for the upgradation of the PAF waste. Recommendations have been made for the utilization of the waste as a substitute for limestone to be used for the neutralization of spent acid, in fluidized bed combustion and for the manufacture of chalk-sticks.

Key words: Analysis, Purification, Utilization, Industrial waste.

Introduction

Disposal of industrial wastes has always been a problem for industries. It has become rather acute all over Pakistan due to lack of effective legislation regarding control of environmental pollution. According to one report seven hundred thousand tons of solid waste is released annually by industries in the country [1]. Besides causing serious disposal problems, industrial wastes are also polluting the environment to harmful levels.

Amongst various processes for environmental pollution control, recycling or utilization of industrial wastes has multiple advantages over the others [2]. In view of this, a number of processes to utilize wastes have been developed in these laboratories by Ali *et.al.* [3-6] and Khattak et.al [7-11]. The present paper is based on studies carried out for the purification and utilization of waste from the Pakistan-American Fertilizer (PAF) Ltd., Iskanderabad, Daud Khel.

Established in 1958, the Pakistan-American Fertilizer (PAF) Plant is a leading fertilizer industry in the country producing 90,000 tons of ammonium sulphate per annum [12]. During the process about 275 tons per day of calcium carbonate is also produced which alongwith some unreacted gypsum and residual ammonium sulphate is discharged in the form of thick slurry around the factory area as shown in Fig. 1. During the last 30 years the deposited waste sludge has covered an area of about 5 square km with a thickness of 5-6 meters of the solid waste (Fig. 2). So far this waste has not found any beneficial utilization except that 50 tons per day is being taken away by the nearby cement plant for the manufacture of white cement [12].

Large quantities of limestone are being used for the waste acid neutralization by some industries in the country. Annual requirement of a single industry (Ittehad Chemicals) is as high as 15000 metric tonnes [13]. In view of these needs and the problem of waste of land, pollution of soil, surface and underground water caused by the PAF Waste, it was considered worthwhile to undertake studies on the purification and some possible utilization of this waste. Details of the studies undertaken and results achieved are described and discussed in this paper.

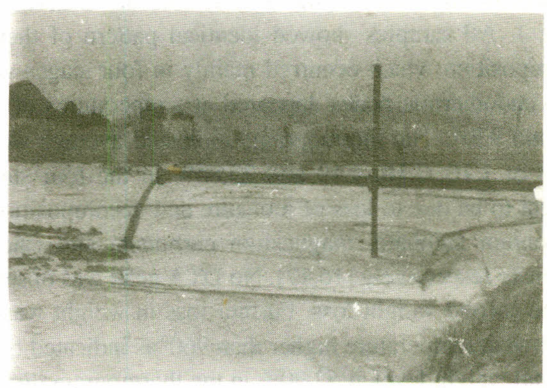

Fig. 1. Waste discharge in the form of slurry at the PAF factory disposal site.

Fig. 2. A part of the disposal site area covered with the thick deposited PAF waste.

Experimental

Samples for analysis were taken at the disposal site of the PAF Plant at Iskanderabad (Daud Khel) in dry weather during May, 1988, from sampling points of waste-slurry discharge. Light cream coloured, dried powdered samples were subjected to chemical analyses without further treatment. The wet chemical analyses were carried by treating the waste samples with concentrated hydrochloric acid using known standard procedures [14].

Thermogravimetry (TG) and Differential Thermal Analyses (DTA) were carried out in an open ceramic crucible under atmospheric pressure at a heating rate of 10° per min. on a Derivatograph (MOM) type thermobalance with automatic recording on photographic Chart.

Sieve analyses was carried out using B.S. Standard sieves. All the chemicals used were of reagent grade quality.

Results and Discussions

Thermogravimetry (TG) and differential thermal analyses (DTA). Thermal studies were carried out on five samples of the PAF waste. The results are described in Table 1. All samples showed identical pattern of thermal decomposition which occurred mainly in four stages while DTA endothermic peaks appeared at temperatures of 130, 815 and 930°. The thermograms indicated average weight losses of 1.10, 2.10, 4.10 and 29.80% in the four stages, thought to be due to loss of moisture and decomposition of ammonium sulphate, magnesium carbonate and calcium carbonate respectively [16,17]. No DTA peak was observed for the second weight loss. Further loss in weight was not observed at temperature higher than 960° as indicated by the constant weight level at 62.90% in the thermogram due to a residue containing a mixture of Oxides and $CaSO_4$.

Chemical analyses. The results of detailed chemical analyses on nine samples of the PAF waste are described in Table 2. As it was also evident from the DT/TGA studies, all the samples appeared to be similar in chemical composition and consisted mainly of calcium carbonate, calcium sulphate and magnesium carbonate. The analytical data obtained from TG/DTA and chemical analyses of the waste samples indicated average calcium carbonate = 74.23%, calcium sulphate = 14.54% and magnesium carbonate = 8.11%.

TABLE 1. TG/DTA RESULTS OF THE WASTE SLUDGE.

Decomposition Temperature (C°)	Weight loss (%) for the PAF samples (1)	(2)	(3)	(4)	(5)	Average
105 - 150 (130)*	1.00	1.25	1.50	1.25	0.50	1.10 ±0.38
190 - 680	1.50	2.25	3.00	1.75	2.00	2.10 ± 0.57
680 - 840 (815)*	4.00	3.50	4.00	4.50	4.50	4.10 ± 0.38
840 - 960 (930)*	28.50	28.00	29.50	29.50	33.50	29.80 ± 2.17
Residue	65.00	65.00	62.00	63.00	59.50	62.90 ± 2.30

*DTA endothermic peak temperatures.

TABLE 2. CHEMICAL ANALYSES OF THE WASTE SLUDGE

Constituent %	Range	Average
Moisture	0.20 - 0.90	0.57 ± 0.29
Loss on ignition	36.04 - 38.20	36.96 ± 0.72
Acid insoluble	1.96 - 2.52	2.20 ± 0.21
Mixed oxides	0.66 - 1.26	1.05 ± 0.23
CaO	46.35 - 49.27	48.01 ± 0.38
MgO	2.61 - 3.06	2.80 ± 0.15
*Sulphate	7.20 - 9.65	8.56 ± 1.10
	Total : = 100.15	

*Results are expressed as SO_3^{-2}

Sieve analysis. The percentage of various fractions of the waste determined by sieve analysis are presented in Table 3 which shows that 96.5% fraction of the sludge consists of particles in the range - 120 to + 340 mesh and only 3.5% fraction passes through 340 size mesh. The largest fraction (cumulative undersize = 67.6%) is between - 250 and + 300 mesh size.

TABLE 3. SIEVE ANALYSES OF THE PAF WASTE

B.S. Mesh. No	Nominal aperture (μm)	Total wt. retained (g)	%Wt. retained	%Wt. cumulative oversize	%Wt. cumulative oversize
100	150	0.0	0.0	0.0	100.0
120	125	0.0	0.0	0.0	100.0
150	105	26.0	2.6	2.6	97.4
200	75	80.0	8.0	10.6	89.4
240	63	218.0	21.8	32.4	67.6
300	53	253.0	25.3	57.7	42.3
350	45	388.0	38.8	96.5	3.5

Purification of the PAF waste with water treatment. In view of the demand of precipitated calcium carbonate, attempts were made to purify the PAF waste to get industrial-grade calcium carbonate.

When the waste was treated with water at room temperature, a small quantity of calcium sulphate was found to be removed from the bulk of calcium carbonate due to its comparatively higher solubility. The effects of stirring time, volume of water and temperature, on the purification of the PAF waste are described in Table 4. Maximum purification was observed when 5 g of the waste sample were stirred for 3 hr. in 250 ml of water at 50-60°. Whereas longer stirring time and larger volume of water did not show any appreciable improvement in the upgradation of calcium carbonate, the increase in temperature to

65° showed less purification due to lower solubility of calcium sulphate in water at temperatures higher than 60° [14,15]. However, only 7% of the impurities could be removed from the waste by this treatment under the stated conditions.

Upgradation with size reduction. Studies were also carried out to see the effect of particle size reduction for the upgradation of calcium carbonate in the PAF waste. Results of DTA/TG and Sulphate analyses of various sieve fractions of the waste are reported in Table 5. Sulphate analyses clearly indicated a decrease in the sulphate content with the gradual reduction in particle size, being 18.45% for the sieve fraction - 120 to + 150 and 3.96% for the sieve fraction from -300 to +340. An increase in the particle size reduction also showed an increase in the calcium carbonate content, as indicated by the weight loss in the temperature range 850 - 960°. Total loss for sieve factions -120 to +150 and -300 to +340 was found to be 30.50 and 41.00%, respectively. The largest fraction lying between -250 and +340 mesh and containing 67.6% of the total fractions showed 78.5% reduction in the original total sulphate content of the waste.

TABLE 4. EFFECTS OF STIRRING, VOLUME OF WATER AND TEMPERATURE ON THE PURIFICATION OF $CaCo_3$ SLUDGE.

Stirring time (hr)	Impurities removed(%)	Solvent (ml)	Impurities removed(%)	Temp (°C)	Impurities removed(%)
(A)		(B)		(C)	
1.00	4.69	50	3.87	18.20	6.47
2.00	5.41	100	5.74	35.40	6.93
2.50	5.42	150	5.83	60.65	7.05
3.00	5.74	200	6.21	75.80	6.63
4.00	5.86	250	6.98	90.95	6.61
5.00	5.97	350	7.11	-	-

1. (A) Volume of water = 100 ml; at room temperature
   (B) Stirring time = 3 hr.; at room temperature
   (C) Volume of water = 250 ml; stirring time = 3 Hr.
2. For all parameters studied weight of sludge taken = 5 g.

TABLE 5. TG AND SULPHATE ANALYSES OF THE WASTE SLUDGE SIEVE FRACTIONS

Sieve fractions (mesh)	Sulphate (%)	110-180 °C	180-760 °C	760-850 °C	850-960 °C	Residue (%)
-120 to + 150	18.45	1.50	2.50	4.00	22.50	69.50
-150 to + 200	11.77	1.00	2.50	3.50	28.00	65.00
-200 to + 250	6.67	1.00	2.50	4.00	31.00	61.50
-250 to + 300	4.70	0.50	2.50	4.00	33.20	59.80
-300 to + 340	3.96	1.00	2.50	4.20	33.30	59.00

It is clear from the results described in Table 3-5 and from the foregoing discussion that further treatment of sieve fraction from -250 mesh (cumulative undersize = 67.60%) with water under the stated conditions, may purify the PAF waste to produce industrial grade calcium carbonate. However, the feasibility studies shall have to be examined carefully for adopting the process for commercial scale production of industrial grade calcium carbonate.

Utilization of the PAF waste for chalk-making. The presence of 74% calcium carbonate and 15% calcium sulphate in the waste sludge suggests its utilization in the manufacture of Chalk sticks. Attempts have therefore been made to convert the waste into a composition suitable for the purpose. In the initial studies, the sludge was subjected to heat treatment at different temperatures and its setting properties were observed. However, practically no setting properties were displayed by the heated material. Therefore, effects of increasing the concentration of anhydrous calcium sulphate were examined by the addition of varying amounts of Plaster of Paris to the waste sludge. Addition of 5-25% Plaster of Paris to the sludge without heat treatment and testing it after 7 days, showed a compressive strength between 100 - 190 psi. The strength of the same mixture varied between 100 - 205 psi when tested after 21 days. The compressive strengths of mixtures were studied after heating the waste sludge at 160° for one hr. This treatment improved the compressive strengths of the material showing values between 100 - 212 psi after 7 days and 105 - 250 psi after 21 days.

TABLE 6. COMPRESSIVE STRENGTHS OF PAF THE WASTE AND PLASTER OF PARIS COMPOSITIONS.

Plaster of paris (%)	Waste sludge %	Compressive after 7 days no heating	Strength (Psi) One hr. heating at 160°C	Compressive after 21 days no heating	Strength (Psi) one hr. heating at 160°C
5.00	95.00	100.00	100.00	100.00	105.00
7.50	92.50	102.50	107.50	102.50	112.50
10.00	90.00	105.00	112.50	110.50	125.00
12.50	87.50	112.50	130.00	125.00	137.50
15.00	85.00	125.00	140.00	140.00	150.00
17.50	82.50	140.00	150.00	160.00	170.00
20.00	80.00	160.00	187.50	175.00	200.00
22.50	77.50	175.00	200.00	185.00	225.00
25.00	75.00	190.00	212.50	205.00	250.00

Having studied the effect of addition of Plaster of Paris on the compressive strengths of waste sludge, observations on the quality of chalk sticks prepared with the same mixture were recorded. Due to the coarser particle size than required for chalk making it was not possible to make good quality chalk stick with the waste. However, with the finer fraction of -300 mesh size, chalk sticks of acceptable quality could be obtained by mixing 20-25% plaster of Paris with the waste which was heated at 160° for one hr. prior to mixing.

Utilization of the PAF waste as limestone substitute. Over the years limestone is in use by a number of industries in Pakistan to neutralize waste acid, produced in various chemical processes. The specifications desired for the purpose are usually off size limestone with 90% or more calcium carbonate content [13]. It is proposed that the PAF waste in the waste fraction of -200 to + 250 mesh size may be used instead of limestone. The waste with particle size between and -100 and + 340 mesh (cumulative under size 100%) was found to consist of 74% calcium carbonate, whereas sieve fraction between - 200 and + 250 mesh (cumulative under size 67.6%) showed an upgradation in the carbonate content as shown in Table 5, by increasing the proportion of $CaCO_3$ to 88%.

It is also proposed that the PAF waste may be used in the recently developed clean coal combustion technology (Fluidized Bed Combustion) in Pakistan [18]. The waste and in particular its fraction between -200 to +250 mesh size may be used as substitute for limestone in the "Desulfurization Bed". However, further studies would be needed to find out the desired specifications of the powdered limestone used in the fluidized bed combuster.

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