Interoffice Correspondence 3M

Subject:

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Comments Please

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The attached report summarizes the current status of research on disposal of hydrofluoric acid tars. In addition, it outlines the course for future work in this program. Your comments and suggestions on this program would be most appreciated.

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Exhibit
1109
State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

The adequate disposal of hydrofluoric acid containing tars poses many problems. The extremely hazardous nature of these materials makes their handling and ultimate disposal difficult and often dangerous. This factor coupled with expansions of processes and product lines which create these wastes has prompted the initiation of a joint effort by the Environmental Engineering and Pollution Control Division and Chemical Division Engineering to seek suitable means for disposal of these tars. The report that follows summarizes the status of this engineering effort and outlines a program of continued study.

BACKGROUND

PROBLEM DESCRIPTION

The manufacture of fluorochemicals at Chemolite and Decatur leads to the formation of a tar-like waste containing hydrofluoric acid. The present generation of these waste tars totals 1300 drums per year; 1000 drums per year from Decatur and 300 drums per year from Chemolite. Additional tars will soon be generated at Cordova and Antwerp, Belgium. Presently, these tars are being stockpiled while an acceptable means of disposal is found. The presence of hydrofluoric acid in these tars makes their handling and disposal outside of the cell buildings hazardous. In addition, stockpiled drums of such corrosive wastes quickly deterriorate in moist environments.

In previous years, tars generated at Chemolite were poured into lime ponds where the free hydrofluoric acid was neutralized. This method of tar treatment resulted in a hazardous situation for those handling the drums and it was often difficult to get adequate lime in contact with the acid. Monitoring of the dry well adjacent to the lime pit showed fluoride ion concentrations exceeding 2800 mg/l and it was decided that the tars should be stockpiled until the pit could be modified or an alternate means of disposal could be found.

Tars generated at Decatur were initially placed into a pit lined with lime. The tars were added in drummed form which decreased the handling hazards. In August, 1973 the landfill area at Decatur was closed because of threats to ground and surface waters from leachate leaving the landfill. The tars have been stockpiled since that time.

EARLY TESTS

L. E. Nelson did experiments with distillation of FM-3108 electrolyte in 1963 in which he added fuming sulfuric acid at concentrations varying from 5-14% of initial charge weight. The idea was that by dissolving the tars in the sulfuric acid, it would be possible to push the distillation to higher temperatures allowing higher HF recovery and recovery of some product intermediates. The data obtained showed some interesting results but the data proved inconclusive with regard to the effect of raising or lowering the level of sulfuric acid. The most favorable data occurred when 14% of the charge weight was fuming sulfuric acid and distillation temperatures of 190°F were used. In this situation, greater than 90% of the charge weight was recovered.

In the fall of 1970, Dean Dworak and Dave Benforado conducted experiments on lime neutralization of HF tars at Bldg. 15. Three experiments were performed in which hot tar bottoms were drained into lime solutions of 13%-19% lime by weight. The reactions were quite exothermic with about 500-600 BTU/lb of tar neutralized liberated. In addition, foaming was observed to be a problem in all but the third run in which the tars were added via a dip tube. The resultant slurry and a muddy water appearance and was sewered for further treatment at the wastewater treatment area.

PRESENT STUDY

The present program to evaluate disposal methods for HF tars is broken into the following:

(1) Lab analyses
(2) Chemolite Incinerator test burn
(3) Sulfuric acid-HF tar distillation
m (4) Line neutralization study
(5) Dryer studies
    (a) Pan dryer study by Don Ware in Allentown, PA.
    (b) Rototherm pilot unit at Chemolite

LAB ANALYSES

Laboratory analyses were performed to suggest approaches for HF tar treatment. In general, the analyses were intended to evaluate (1) direct incineration, (2) lime neutralization, or (3) tar drying. Most of the analyses were performed on FM 3330 tars from Decatur since this tar represents approximately 75% of present tar generation. Typical analyses (each batch of tars is slightly different depending on distillation conditions) for the FM 3330 tars are shown below:

Analysis	Value
Total Fluorine	59% by weight
Free Fluoride	28% by weight
Leachable Fluoride after air drying	65.5 mg F^-/gm dried tars
Leachable COD after air drying	9.85 mg/gm dried tars
Leachable BOD_5 after air drying	No depletion (Nonbiodegradable)
Leachable COD after hot plate drying	2.15 mg/gm dried tars
Leachable BOD_5 after hot plate drying	No depletion (Nonbiodegradable)
Leachable Fluoride after hot plate drying	19.5 mg F^-/gm dried tars
BTU/lb on air dried residue	6,351
pH of 5-1 water slurry of air dried tars	0.8
pH of 5-1 water slurry of hot plate dried tars	2.3
75/25 mixture of FM 3330 tars/conc. H_2SO_4 heated to 200°F.	
(1) Leachable Fluoride	24.2 mg F^-/gm mixed tar-H_2SO_4 paste
(2) COD	44.0 mg/gm
pH of FM 3330 tars after lime neutralization	3.2
Leachable Fluoride after lime neutralization	0.54 mg F^-/gm filter cake
Leachable COD of filter cake after lime neutralization	4.25 mg/gm filter cake (59.2% H_2O)
Leachable BOD_5 of filter cake after lime neutralization	0.16 mg/gm filter cake (59.2% H_2O)

Discusssion of laboratory analyses: From the analyses performed in the laboratory it appeared that both lime neutralization and forced drying of the FM 3330 tars could yield a satisfactory end product from the view of disposal. The lime neutralization and sulfuric acid addition were highly exothermic and difficult to control on a laboratory scale. Much foaming occurred in the lime neutralization tests regardless of whether the 20% lime slurry was added to the tar or the tar added to the lime slurry. Some HF was known to have evaporated directly into the hood but it is not believed to have been enough to significantly alter the analytical results. Larger scale tests were needed to resolve the feasibility of these methods for HF tar treatment.

CHEMOLITE INCINERATOR TEST BURN

In October, 1973 two test burns were made at the Chemolite incinerator using K-300 tars chosen at random from the stockpile area. The complete report is attached as Appendix A. In summary, the tests were designed to burn tars at the maximum charging rate (14 drums/hr for these tars) and at a more moderate rate (8 drums/hr) while monitoring combustion gases before and after the air pollution train as well as the scrubber water exiting the quench chamber. The results showed an average (over four test periods) of 88 mg F^-/ft^3 leaving the secondary combustion chamber (at 60,000 CFM this equals about 11.6 lb F/minute entering the air pollution section) and 13.9 mg F/ft^3 exiting the stack (at 16,000 CFM this equals 0.49 lb F^-/min). In addition, an average fluoride reading in the quench water of 8078 mg/l was observed with a subsequent corrosion probe reading of nearly 1000 mm/year (static). From these data it can be expected that burning HF tars in the Chemolite incinerator will cause corrosion and perhaps refractory damage but that the scrubber system on the incinerator can successfully keep the large quantity of fluoride from reaching the atmosphere in an amount harmful to the environment. Because of heavy use for this incinerator, however, it can not be recommended as a disposal source for continuously generated tars in the future although it may be possible to slowly burn stockpiled tars. Mike Santoro is considering this possibility at the present time. See Appendix B for Central Research evaluation of HF on the mortars and refractories in the incinerator.

LIME NEUTRALIZATION

In January, 1973, one hundred pounds of FM 3109 tar was slowly added to an agitated 55-gallon drum containing a 20% lime slurry in quantity 100% in excess of that required to neutralize one hundred pounds of an HF tar containing 20% free HF. The neutralization was done over about a one hour period of time. No violent exothermic reaction or foaming was observed due to the slow rate of addition of tar to the lime slurry. Fuming was not observed. The following analyses were run:

FM 3109 Lime Neutralization

Analysis	FM 3109 Tar	Lime Filter Cake	Filtrate Liquid
% H_2O		47.6%	
Total Fluorine	41.8%		
pH		1 (litmus)	0.28
Fluoride Ion (water)			23,750 mg/l
COD (water)			9,520 mg/l
COD (leached)	59 mg/gm	9.0 mg/gm	
Fluoride Ion (leached)	400 mg/gm	16.25 mg/gm	

This would suggest that the filter cake resulting from lime neutralization of FM 3109 is quite low in leachable pollutants but that the filtered liquid stream has high COD and F^- concentrations and may require further treatment as a wastewater stream.

The FM 3109 lime treated tars were submitted to Chemfix for evaluation as to the possibility of chemically fixing this slurry if the necessity arises. Their conclusion was that it could be stabilized for a cost of from 5¢/gallon to 9.5¢/gallon depending on slurry volume. See Appendix C for proposal.

In March, 1973, two lime neutralization runs were made at Bldg. 16 Chemolite in the 10 gallon monel jacketed reactor system. The first run consisted of lime neutralizing FM 3330 tars from Decatur and the second run lime neutralizating F 4841 (Agrichem) tars. In both tests, the tars were vacuum charged to the reactor and lime slurry (20% by weight) was slowly added to neutralize the free HF while the reactor was simultaneously agitated and cooled. Lime slurry was added in about 100% excess to give a neutralized pH of approximately 10. The temperature of the batch never exceeded 125°F on either run. Physically, 14.7# of FM 3330 tars were neutralized by 11.7# of $Ca(oH)_2$ in 47# of D.I. water while 14.7# of F 4841 tars required 17.6# of $Ca(OH)_2$ in 70# of D.I. water for neutralization to pH 10. The laboratory analyses on the resulting filter cakes and supernatants are as follows:

Analysis	FM 3330 Filter Cake	FM 3330 Supernatant	F 4841 Filter Cake	F 4841 Supernatant
Total Solids @ 103°C	79.7%		40.3%	
Water %	20.3%		59.7%	
Leachable COD	10.2 mg/gm		57.0 mg/gm	
Leachable BOD	562 mg/1		2250 mg/1	
Leachable F^-	103 mg/gm		96 mg/gm	
pH	10 (litmus)	12.31	10 (litmus)	11.65
Soluble solids		0.65%		9.02%
Fluoride		199 mg/1		380 mg/1
COD		5760 mg/1		45,600 mg/1
BOD_5		1125 mg/1		11,250 mg/1
Sulfur		0.1%		2.0%

The analyses would suggest, as in the earlier test, that the filter cakes are probably landfillable (the F 4841 filter cake is questionable) but that the supernatants will require further treatment.

DRYER STUDIES

On June 6 and 7, 1974, tests were performed at the Bethlehem Corporation laberatiries in Bethlehem, Pennsylvania. These tests were arranged for and supervised by Don Ware from Decatur Chemical and were designed to evaluate the ability of a pan dryer to dry FM 3330 tars to a solid state. The tests were run at elevated temperatures ranging from 250°F to 300 °F under essentially atmospheric pressure. In the first test, tars were added to a depth of approximately five inches. They were then slowly agitated and heated. After two hours, the tars had dried to a rubbery consistency and had balled up on the agitator. Upon continued heating, the tars dried to a powder form. In the second test, the tars were added to a bed of the dried residue from the first test in a weight ratio of roughly 75% residue/25% tar. This material dried readily and offers much hope for a successful method to dry HF tars. Don plans to continue his work with a dryer of superior design in August, 1974.

In May and June, 1974, a thin film evaporator was piloted at Chemolite Bldg. 15 to evaluate the feasibility of using this type of dryer to remove HF from various electrolytes and tars. The unit used in this evaluation was a one square foot Rototherm E rental unit manufactured by Artisan Industries. It was a horizontal design with a "paddlewheel" rotor having about 1/16" wall clearance. It had a variable speed drive with rotor speeds varying form approximately 600 RPM to 1600 RPM. General descriptive information is enclosed in Appendix D.

A number of unsuccessful attempts were made to operate the unit on FM 3109 electrolyte under 12-20 pounds of pressure. In each case plugging of feed lines or flooding of the unit caused us to terminate the runs. When cleaning up the dryer following these runs we would find dried solids in the unit even though the residue hopper contained much liquid tar. This indicated to us that the unit was working during periods of operation but that we were flooding the unit often enough to redissolve the dried particles reaching the residue hopper. This belief was reinforced by observations of solid lumps in the residue liquid. On several runs it was observed that greater than 80% of the total weight charged was vaporized and recovered in the condenser. Normally such a reduction in weight would result in a solid residue (the K-300 still, for example, takes a 2000 lb electrolyte charge down to 600 lb residual or a 70% weight reduction). The only explanation for this observation would be that either we are breaking down and liquifying the tar solids or we ran electrolyte containing atypically low solids content. Analyses on collected samples are in progress.

On June 18, 1974, we ran drying tests with the Rototherm unit on FM 3330 tars with a shell temperature of 250°F and under vacuum 20 inches Hg. Approximately 65# of tars were charged at a rate of roughly 0.1 GPM. The feed line plugged on several occassions and back pressure was used on the line to free it of the plug. Near the conclusion of the test we had a period of operation approaching 0.5GPM feed rate which probably flooded the small pilot unit. Upon opening the receiver we found a liquid residual with many solid lumps. Following draining of the hopper we dismantled the equipment and found it full of dry residue. Samples were taken for analyses. On June 19, 1974, we reran the test of the previous day taking care not to exceed 0.1 gpm feed rate.

Plugging of the feed line was a problem throughout, After processing 36# of tar we terminated the run. Completely dry residue was found in the residue hopper. This, therefore, constituted our only successful test run. Samples were taken for analyses and the testing of this unit was terminated.

From our experiences with the Rototherm dryer we concluded that such a dryer can work on drying tars when the feed rate is very slow. Such a unit, being of horizontal design, is unacceptably vulnerable to flooding with even brief surges of high flow. It is our opinion that continued experimentation with the thin film evaporator should be carried out with a vertical unit. Nevertheless, the Rototherm equipment has demonstrated that such an approach to tar drying is possible and valid.