

CONTROL TECHNOLOGY ASSESSMENT OF HAZARDOUS WASTE
DISPOSAL OPERATIONS IN CHEMICALS MANUFACTURING

IN-DEPTH SURVEY REPORT

OF

SAN JUAN CEMENT COMPANY
DORADO, PUERTO RICO

SURVEY CONDUCTED BY:
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Michael S. Crandall

DATE OF SURVEY:
November 1981

REPORT WRITTEN BY:
Michael S. Crandall

DATE OF REPORT:
July 1982

REPORT NO.:
ECTB 103-21a

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Physical Sciences and Engineering
Engineering Control Technology Branch
4676 Columbia Parkway
Cincinnati, Ohio 45226

PURPOSE OF SURVEY: To conduct an in-depth study of hazardous waste disposal operations in chemicals manufacturing with a view to documenting exemplary controls.

EMPLOYER REPRESENTATIVES CONTACTED: Juan Alberto Valls, Plant Manager
Arturo J. Guerrero, Safety and Impac Manager

EMPLOYEE REPRESENTATIVES CONTACTED: None

EPA REPRESENTATIVES CONTACTED: Robert Mournighan, EPA
Douglas Hazelwood, Associate Consultant
A. T. Kearny, Inc.

STANDARD INDUSTRIAL CLASSIFICATION
CATION OF PLANT: Hydraulic Cement
(SIC 3241)

ANALYTICAL WORK PERFORMED BY: WBTL, Salt Lake City, Utah
Adith Grote, MSRB, NIOSH

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) (PL-94-580) of 1976 was enacted to provide technical and financial assistance for the development of management plans and facilities for the recovery of energy and other resources from discarded materials, for the safe disposal of discarded materials, and to regulate the management of hazardous waste. Under Subtitle C of RCRA, the Environmental Protection Agency (EPA) was required to promulgate regulations on identification and listing of hazardous wastes and regulations affecting the generators, transporters, and owners/operators of facilities for the treatment, storage, and disposal of hazardous wastes. These regulations appeared in the Federal Register on May 8, 1980. Amendments affecting the listing of hazardous wastes appeared in the Federal Register November 12, 1980.

There are between 35 and 60 million tons of hazardous wastes generated annually, of which about 15 million are generated by industries in the Chemical and Allied Products Sector (SIC 28). These wastes contain toxic substances which may also be carcinogenic, mutagenic, and teratogenic. Some of the companies in SIC 28 treat, store, and dispose of the wastes that they generate. Wastes may also be transported to companies who specialize in the treatment, storage, and disposal of these wastes. This group of companies is classified as "Refuse Systems" (SIC 4953). It is estimated that about 6,200 workers are directly involved in the transportation, treatment, storage, and disposal of hazardous wastes from SIC 28.

There are many companies in both SIC 28 and SIC 4953 which are currently treating and disposing of hazardous wastes from chemicals manufacturing. Many of these companies have controls in place that are designed to protect the workers from known hazards, both during normal operations and during upsets or emergencies. The objective of this control technology study is to document and disseminate information on effective engineering controls, work practices, monitoring programs, and personal protective equipment. The NIOSH study will result in a technical report designed to assist hazardous waste operators in their efforts to prevent worker exposures to occupational health hazards.

Furthermore, an attempt will be made to present a spectrum of available alternatives for hazard control in various treatment and disposal operations.

The implementation of RCRA regulations has created business opportunities in the area of hazardous waste treatment and disposal. This has also created employment opportunities reflected by a steady rise in the number of workers who are involved in the treatment and disposal of hazardous wastes.

The Occupational Safety and Health Act of 1970 (PL-91-596) was enacted to "assure safe and healthful working conditions for men and women." The Act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health and Human Services. NIOSH was charged by this Act with the duty and responsibility to conduct research and develop guidance for preventing exposure of workers to harmful chemical and physical agents. In response to this legislative mandate, NIOSH has conducted major programs to document, develop, and disseminate information regarding the health effects of such agents. To complement these ongoing programs, NIOSH has instituted a major effort to prevent occupational health and safety problems through the assessment and application of control technology in the workplace.

This in-depth survey was conducted with the cooperation of the U. S. Environmental Protection Agency (EPA). The EPA was conducting a pilot project aimed at: (1) demonstrating the feasibility of burning organic wastes containing chlorinated hydrocarbons in a cement kiln; and (2) complete characterization of the stack emissions. The intent of NIOSH was to determine the effectiveness of hazard control technologies used during this demonstration project. The wastes to be burned were supplied by an Inland Chemical Corporation plant located in Puerto Rico.

AUTHORITY

Two of the main policy objectives of the 1970 Occupational Safety and Health Act (PL 91-596) are to:

- o Encourage employers and employees in their efforts to reduce the number of occupational safety and health hazards at their places of employment, and to stimulate employers and employees to institute new and to perfect existing programs for providing safe and healthful working conditions.
- o Provide for research in the field of occupational safety and health with a view to developing innovative methods, techniques, and approaches for dealing with occupational safety and health.

Under Section 20 of the Act, the Secretary of Health and Human Services is authorized to conduct special research, experiments, and demonstrations relating to occupational safety and health as are necessary to explore new problems including those created by new technology.

Paragraph (d) requires the dissemination of the information obtained to employers and employees.

The National Institute for Occupational Safety and Health was established to perform the functions of the Secretary of Health and Human Services described in Sections 2 and 20 of the Act. The manner in which investigations of places of employment are conducted by NIOSH and its representatives is outline in the Code of Federal Regulations (Title 42, part 85a).

PLANT DESCRIPTION

San Juan Cement has operated a cement plant in Barrio Espinosa in Dorado, PR since 1970. Figure 1 is a map showing the location of the plant.

San Juan Cement is dedicated to the manufacture of Portland cement. It is the second largest cement plant in Puerto Rico. Annual production averages 450,000 tons per year and employment is 350 workers year round.

The plant facilities consist of quarries from which raw materials are extracted; grinding and blending operations for preparing a properly proportioned mixture of raw materials; three wet-process rotary kilns which convert the raw materials into cement clinker; grinding mills in which the clinker is finely ground and mixed with gypsum to form the cement product; storage, bagging, and material transfer equipment; and office, maintenance, dust disposal, and related areas. Figure 2 shows the general plant layout including the major equipment at the site.

The EPA demonstration project required that additional equipment be installed at the plant for storing and pumping the supplemental hazardous waste fuels to be used. The location of this equipment is indicated by dotted lines in Figure 2.

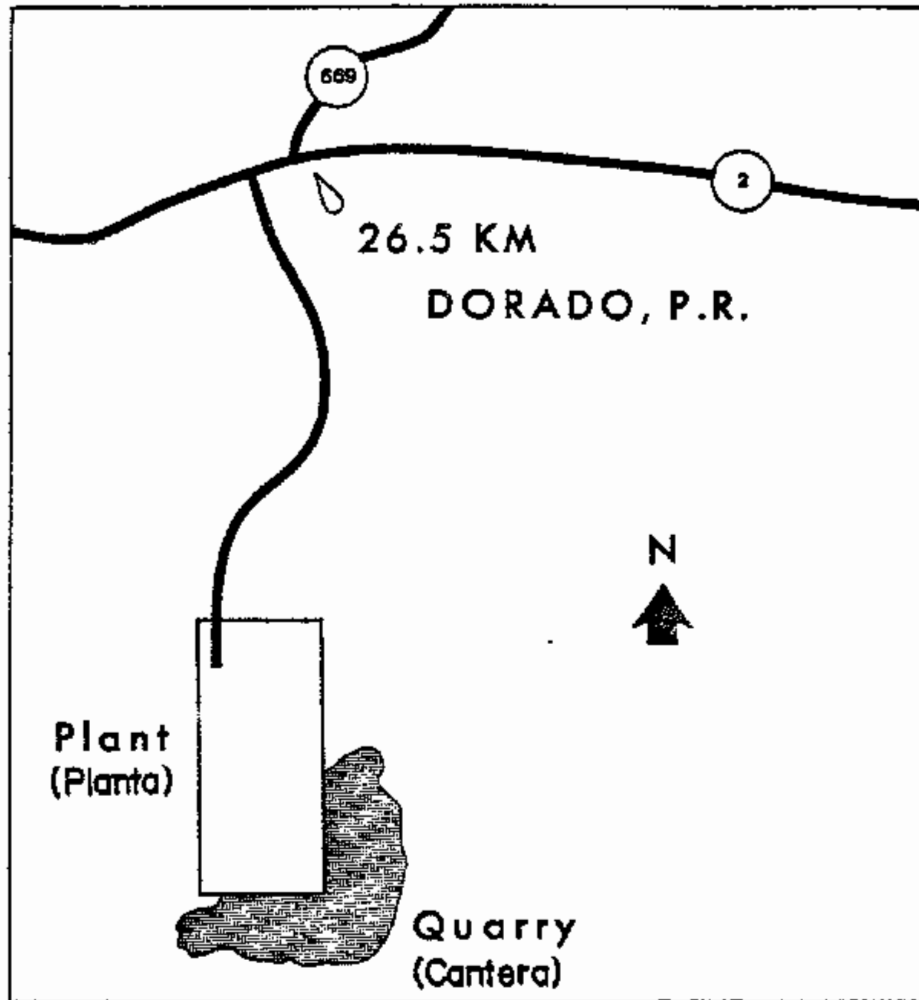


Figure 1. Plant location.

KM 26.7 STATE HIGHWAY NO. 8 DORADO, P.R.

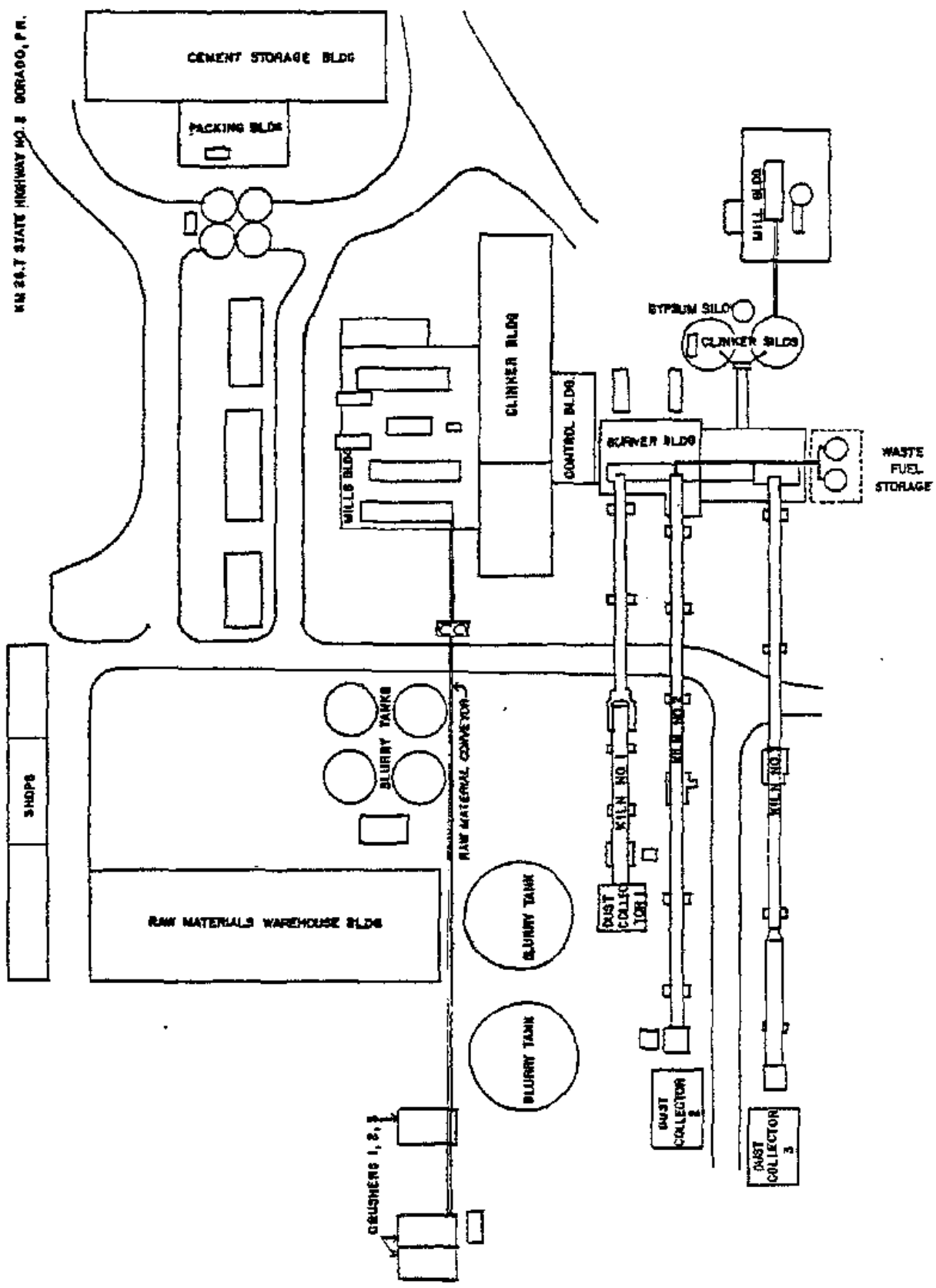


Figure 2. Waste fuel storage site.

PROCESS DESCRIPTION

The process surveyed was a storage and delivery system for hazardous wastes being used in a demonstration project as a supplemental fuel for co-firing a cement kiln. Figure 3 is a diagram of the equipment set-up for this process.

Two 10,000 gallon steel storage tanks were placed on an impermeable concrete slab installed in the area adjacent to kiln No. 3. This slab was surrounded by a sealed retaining wall so that a potential spill would be completely contained.

Pumps were installed near the storage tanks to transfer the supplemental fuels. A low pressure centrifugal pump was used to fill the storage tanks from the tanker delivering the waste fuel at approximately 190 gallons per minute (GPM). A positive displacement pump operating at approximately 200 pounds per square inch pressure was used to transfer the fuels into the kiln at approximately 5 GPM. There was a back-up pump adjacent for this operation.

Steel piping with all-welded joints was used to carry the waste fuels from the storage tanks to the kiln. This system was valved at the storage tanks and at the kiln firing area to allow for flow cut-off at either location. Figure 4 is a schematic of this system.

The supplemental fuels were injected into the kiln through a specially-fabricated burner inserted next to the existing fuel oil burner and were not mixed with the fuel oil. A schematic drawing showing the liquid fuel and vapor flows is presented in Figure 5. The vapor emitted from the tanks as a result of breathing (thermal expansion and molecular diffusion) during storage was vented into an activated carbon sorbent bed.

Vapor emissions from the tanks during routine filling operations were suppressed by venting the displaced vapor from the storage tanks directly into the tank truck through a recycle line. A schematic of the storage tank filling operation is in Figure 6.

Kiln No. 2 is the only equipment at the site in which waste fuels were burned during the demonstration. Exhausts gases from this kiln pass through a bag-house-type dust collector where entrained particulates are removed. The cleansed exhaust gases are then released to the atmosphere through a single stack.

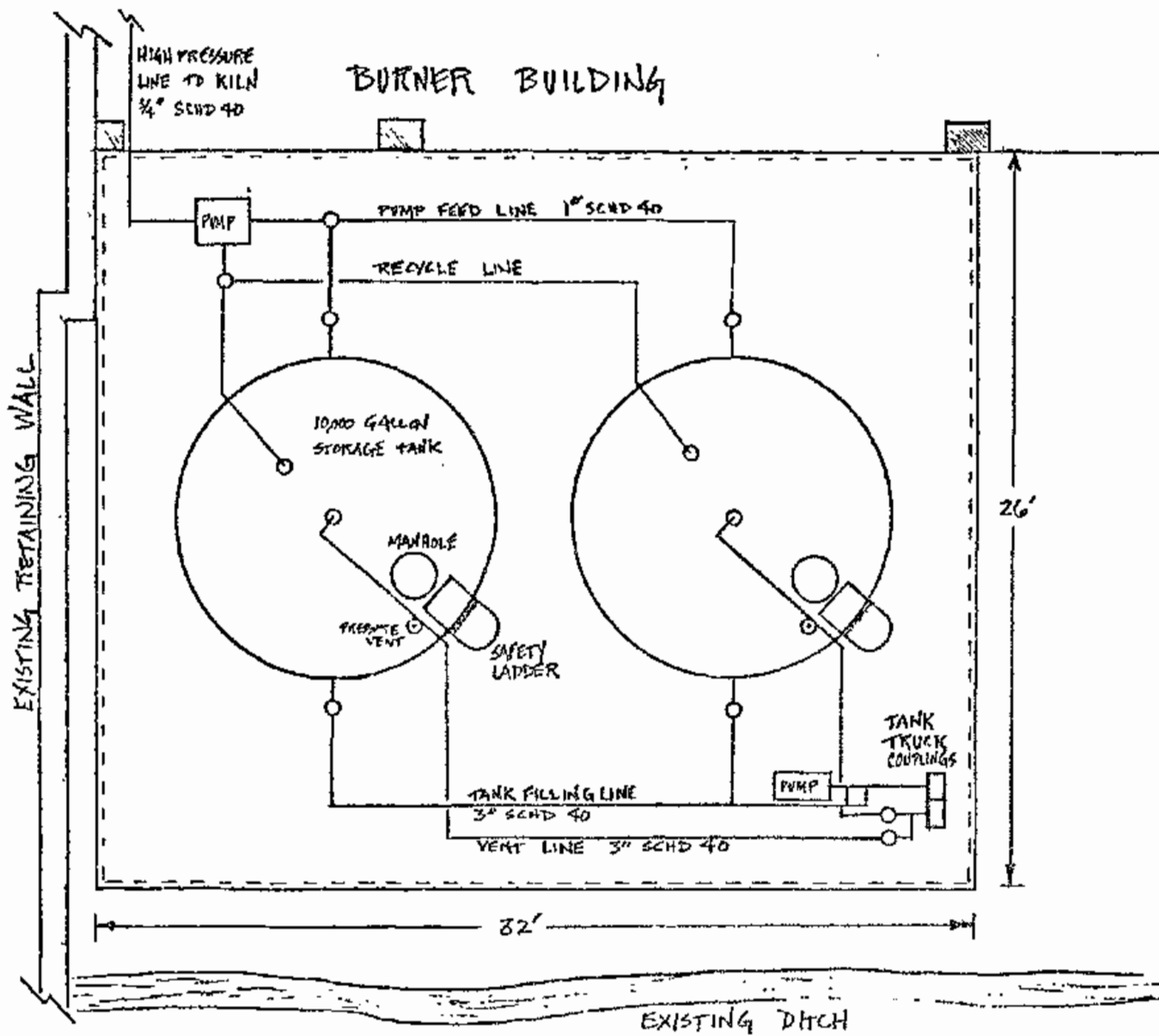


Figure 3. Recycled fuels storage/delivery system.

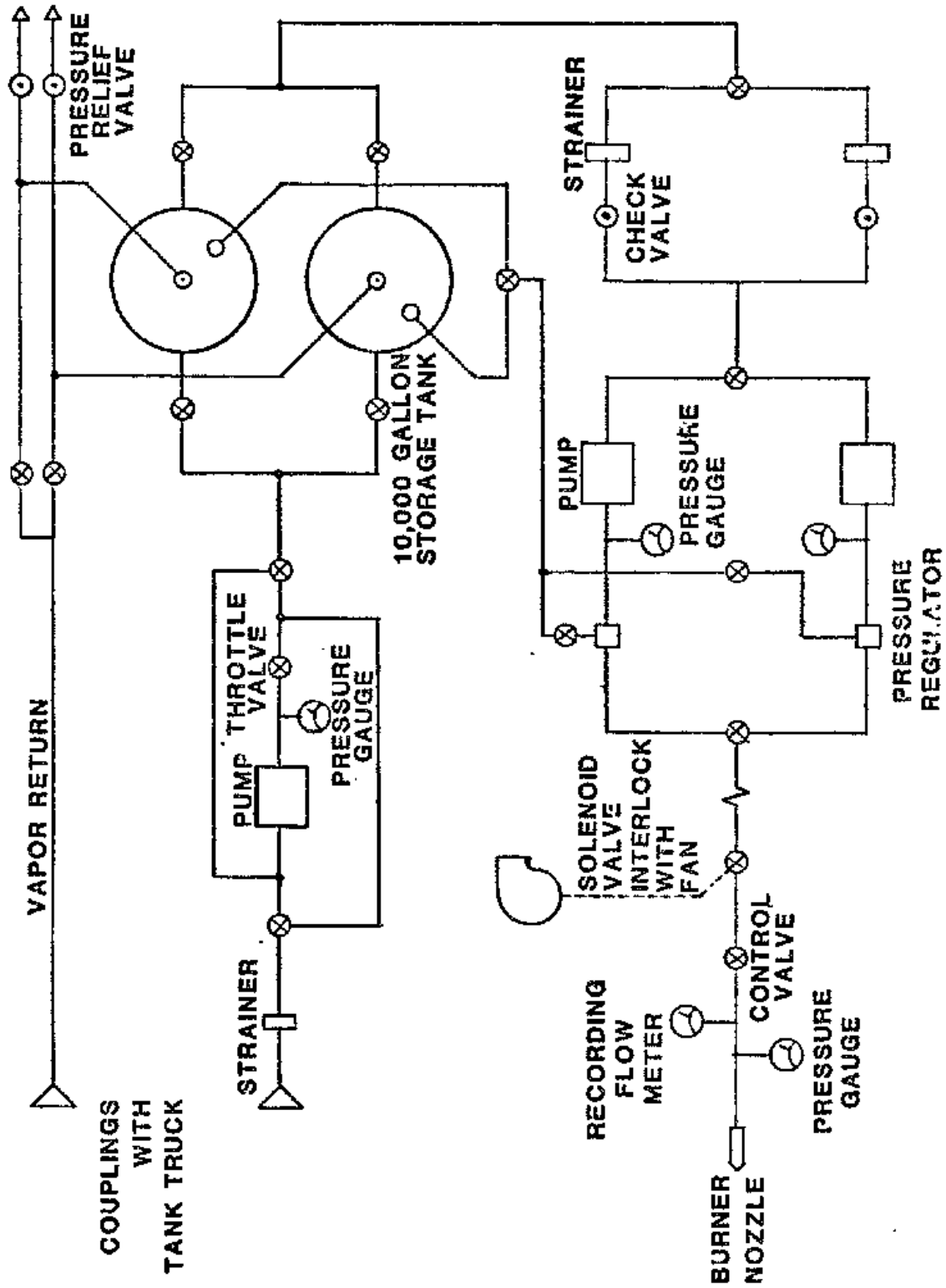


Figure 4. Recycled fuel handling system.

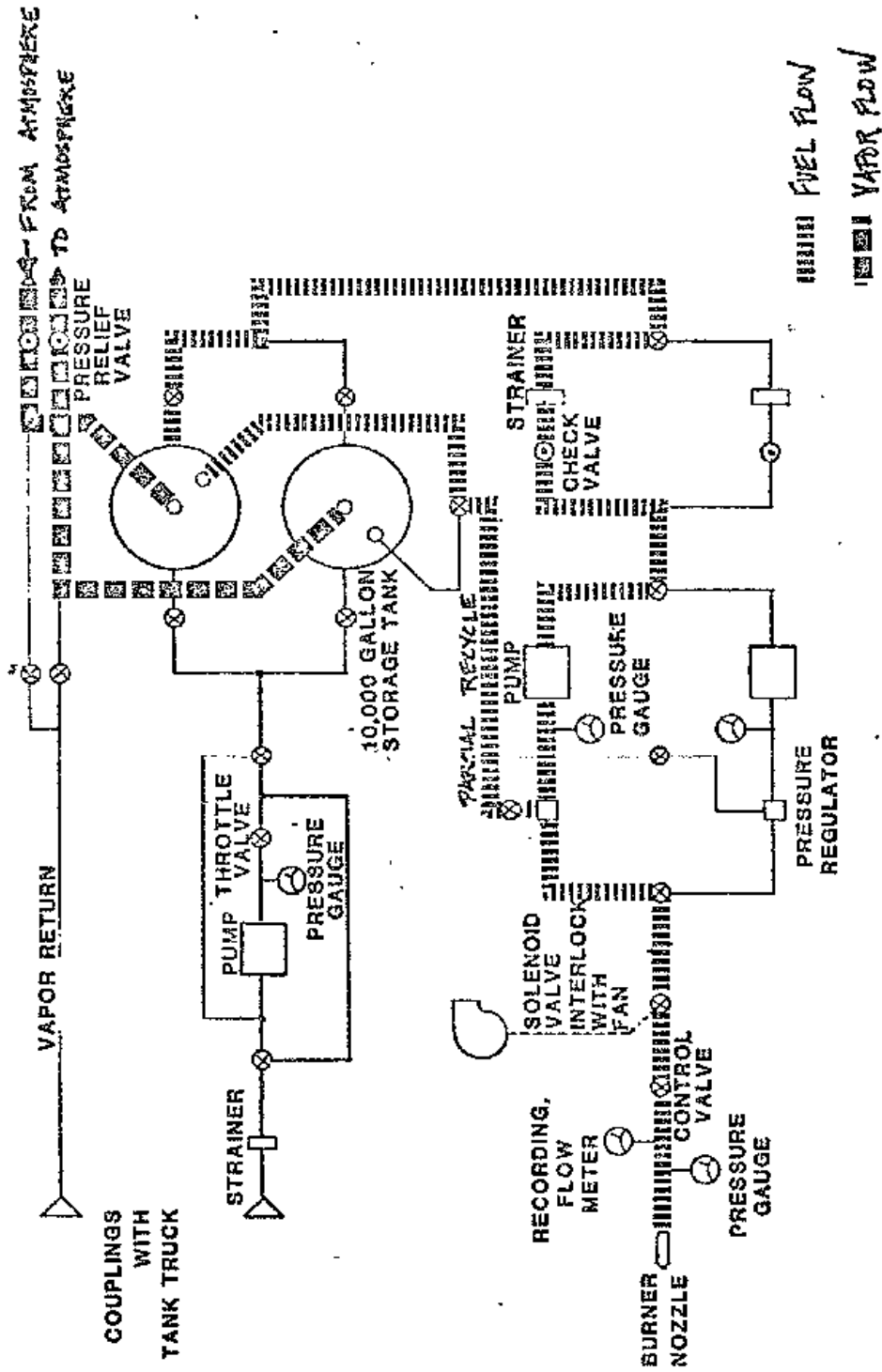


Figure 5. Flows during use of recycled fuels.

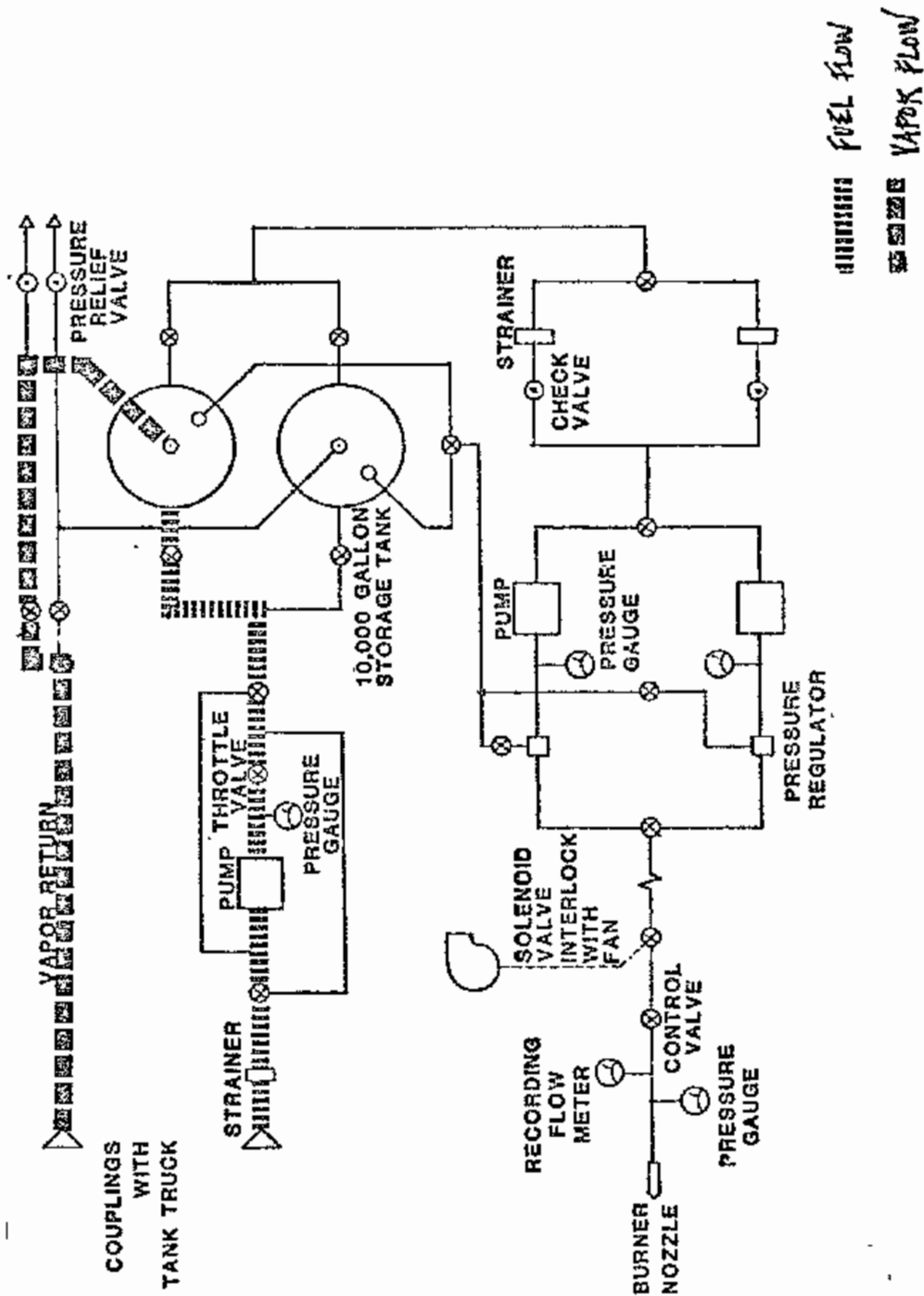


Figure 6. Flows during tank loading.

HAZARD EVALUATION

Exposure to the hazardous waste mixture being used as supplemental fuel was to be evaluated. The health effects due to this exposure are as yet unknown. These mixtures are highly toxic and may often contain carcinogenic or suspected carcinogenic materials. Percutaneous absorption of the liquid or vapor, and inhalation of the vapor were the possible routes of exposure.

During this demonstration, intense exposures of short duration were of more concern than the constant low level variety. These would likely occur during material transfer from tanker trucks to storage tanks, spills and leaks, and maintenance activities, such as cleaning filters and strainers in fuel lines.

Analyses of the hazardous wastes used as supplemental fuel during the NIOSH survey are in Table 1 as provided by the EPA. The major components were methylene chloride, carbon tetrachloride, chloroform, acetone, hexane, ethanol, and ethyl acetate.

Bulk liquid samples were taken from each batch and submitted to NIOSH for analysis. Both bulk distillate and head space vapor (@ 30°C) were analyzed by GC/MS. The components identified on the total ion chromatogram from the bulk distillates are presented in Table 2. These analyses identified methylene chloride, hexane, and ethyl acetate as major components in both batches. Chloroform and carbon tetrachloride were also identified as major compounds in Batch 4.

Table 1. Summary of Waste Fuel Analyses for San Juan Cement Demonstration Burn (weight basis).

Compound	Batch #3 wt %	Batch #4 wt %
Water	4.6	8.8
Methanol	11.9	4.8
Ethanol	7.3	3.7
Acetone	9.5	8.2
2-Propanol	4.5	3.5
Methylene chloride	17.2	15.8
Hexane isomers	1.3	1.0
3-Methylpentane	1.9	2.1
Hexane	5.1	5.5
Chloroform	5.4	7.9
Ethyl acetate	8.7	5.9
Methyl acetate	0.4	0.9
Carbon tetrachloride	2.4	16.1
Benzene	0.2	0.3
Hexamethyl disiloxane	ND	NA
Toluene	0.02	0.4
Acrylonitrile	1.0	0.6
Methyl ethyl ketone	0.06	0.9
C ₅ -Benzene isomer	1.3	0.4
C ₆ -Benzene isomer	ND	NA
Sec-butyl ethylbenzene	1.2	1.5
Xylene isomers	0.2	NA
Dimethylphenol isomer	0.04	NA
1,1'-(1,2-ethanediol)bis-4-methoxybenzene	0.2	NA
Unknowns	15.4	11.7

Table 2. Components of hazardous wastes used as supplemental fuel identified by NIOSH GC/MS analysis.

Batch No. 3	Batch No. 4
Methanol	Methanol
Ethanol	Ethanol
Acetone	Acetone
Isopropanal	Isopropanal
Ethylacetate	Ethylacetate
Methyl acetate	Methyl acetate
Methylene chloride	Methylene chloride
C ₆ H ₁₄	C ₆ H ₁₄
2-Methyl pentane	2-Methyl pentane
3-Methyl pentane	2-Methyl pentane
Methyl ethyl ketone	Methyl ethyl ketone
n-Hexane	n-Hexane
Chloroform	Chloroform
C ₆ H ₁₂ (Methyl cyclopentane)	C ₆ H ₁₂ (Methyl cyclopentane)
Benzene	Benzene
Carbon tetrachloride	Carbon tetrachloride
Butanol	Butanol
Pyridine	Pyridine
Toluene	Toluene
N,N-dimethylformamide	N,N-dimethylformamide
n-Butylacetate	n-Butylacetate
Xylene	Xylene isomers
Methyl cellosolve	

CONTROL TECHNOLOGY

The basic elements of control technology which are implemented to minimize or eliminate hazards in the workplace are: (1) engineering controls; (2) industrial hygiene and medical monitoring; (3) training and education that result in effective work practices; and (4) personal protective equipment.

ENGINEERING CONTROLS

Vapor emissions were controlled by means of a recycle line and a carbon adsorption bed on the hazardous waste storage/delivery system. Two modes of operation were available for vapor suppression. During normal pumping and kiln downtime, the vents in the storage tank tops were valved to the carbon bed for organic vapor adsorption prior to breathing to the atmosphere. During the storage tank filling operation, the vents were valved to the recycle line to the tank truck preventing the displaced vapor from escaping to the atmosphere, or overloading the carbon bed.

INDUSTRIAL HYGIENE AND MEDICAL MONITORING

Worker industrial hygiene monitoring for hazardous organic vapor was conducted by NIOSH during this survey. If San Juan Cement purchases the operation, this type of monitoring should be on a routine basis.

WORK PRACTICES

Training employees to follow work practice guidelines which are safe and effective in preventing unnecessary exposure is imperative when handling hazardous wastes. There was no training program as such at San Juan Cement since this was a demonstration project conducted by an outside agency. If this operation is purchased by San Juan Cement for continued use, such training should be policy.

PROTECTIVE EQUIPMENT

Half-mask air purifying respirators with NIOSH-approved organic vapor cartridges were used when in the hazardous waste storage/delivery area. Best Neoprene #6797 gloves were used when performing a task which might result in skin contact with the liquid. Other safety equipment included hard hats, safety glasses, and safety shoes. The climate discouraged the use of long-sleeved work clothing. In more temperate zones they would be required.

SAMPLING METHODOLOGY

EQUIPMENT

Charcoal tube sampling is considered a most reliable and effective method for determining airborne levels of organic vapors and was the method used to collect all personal and source samples at San Juan Cement.

Personal, full-shift time-weighted average (TWA) sampling was conducted using MDA Model 808 sampling pumps. The sampling flow rates were determined by using 50 cc/min limiting orifices. Two 150 milligram (mg) charcoal tubes were used in series for organic vapor sample collection in order to minimize the possibility of breakthrough, and eliminate sample migration. The entire front tube served as the sample adsorbing section and the second tube acted as a breakthrough indicator (greater than 25 percent of the total sample in this section indicates breakthrough). The two tubes were joined with a short piece of Tygon^(R) tubing, and were connected to the sampling pump with a longer section of tubing which allowed for ample freedom of movement for the worker with the sampling apparatus in-place.

Short-term personal and stationary source sampling (15 to 30 minutes) was conducted using DuPont P-4000 sampling pumps. These were calibrated prior to the survey at a nominal 1.0 liter per minute (Lpm) flow rate. Spot checks were made in the field to assure calibration. Organic vapor samples were collected using the same media configuration as mentioned above.

ANALYSIS

The 13 samples collected at San Juan Cement and 6 field blanks were submitted for analysis to UBTL, Salt Lake City, Utah. All sample tubes were analyzed for the presence of methylene chloride, chloroform, carbon tetrachloride, and N,N-dimethylformamide (DMF). These compounds were chosen on the basis of the previous bulk distillate GC/MS results. The three chlorinated species were

chosen because they were relatively abundant in both batches. The DMF was chosen as a check on the sensitivity and versatility of the analytical method.

The charcoal tubes were analyzed by gas chromatography with a flame ionization detector using NIOSH method P&CAM 127 with modifications. These modifications are listed in the analytical report in Appendix A, along with all analytical results. The detection limits for the requested analyses were 0.01 mg per sample for each analyte.

SAMPLING RESULTS

The results of all TWA and source-samples collected are presented in Table 3. All sample results were below applicable standards. The only significant exposures found were to methylene chloride and carbon tetrachloride. Samples S-1, S-2, and S-9 were the only ones near or above 10 ppm of either substance. All were personal source samples.

Sample S-1 was collected over a 15-minute period, while the worker was returning approximately 5 gallons of waste collected from various leaks to the storage tank. This was accomplished by removing the top cover of the inlet strainer and manually pouring the waste in. The strainer was also cleaned at this time.

Sample S-2 was collected in 15-minutes, while the worker was preparing the system for start-up. During this time the strainer between the storage tank and the pump was inspected and the pump was activated for prestart-up recycle and line pressure adjustment.

Sample S-9 of 10-minute duration was collected while getting a bulk liquid sample of Batch No. 4 out of the South storage tank. It was necessary to return part of this to the storage tank through the inlet strainer. The inlet line was under a slight positive pressure which resulted in a small spill upon opening. Sample S-3 was collected during the performance of a similar task. Pressure had been relieved in the line at some time prior to opening and no spill occurred, resulting in no significant exposure. This points out the importance of following proper routine work practices. The pressure should have been relieved prior to opening this inlet line.

Three of the results (samples S-5, S-6, and S-8) showed breakthrough. An explanation is not straightforward. Sample S-5 was collected during the tanker truck disconnect procedure after storage tank filling. A spill happened when the inlet strainer was checked during this procedure. This could have created

a large vapor dose which was pulled through the first tube (in a chromatographic fashion) due to the high flow rate. Sample S-6 was collected over a long time period (42 mins.) at a high flow rate (1 Lpm). It is possible that displacement of the chlorinated species could have occurred.

The American Conference of Governmental Industrial Hygienists recommends that "when two or more hazardous substances, which act upon the same organ system, are present their combined effect should be given primary consideration."¹ The formula presented in Reference 1 was used to calculate the additive TLV^R for each sample collected.

$$\text{(Additive TLV}^R = \frac{C_1}{\text{TLV}_1} + \frac{C_2}{\text{TLV}_2} + \dots + \frac{C_n}{\text{TLV}_n}$$

When the sum of these fractions exceeds unity, the TLV for the mixture is considered as being exceeded.)

Samples P-2 and S-1 both approached the limit of unity. Sample S-1 collected on the same person on the same day as sample P-2, reflects a contributing short-term exposure to sample P-2.

Tables 4 and 5 display the ranges of exposure for all analyses and permissible exposure limits.

It was of interest to determine personal exposure to all components in the vapor phase of these hazardous waste mixtures. By evaluating the exposure to several abundant substances it was hoped that the exposure to the total mixture may be arrived at. The total vapor phase composition could not be determined in the laboratory analysis, so an assumption was to be used that it equalled the liquid phase composition. However, the magnitude of airborne concentrations found did not correlate with the known liquid phase, and this approach was abandoned.

Table 3. Organic vapor sampling results for the San Juan Cement hazardous waste fuel demonstration.

Sample #	Field #	Vol. (l)	Job Title/Task	Methylene Chloride		Carbon Tetrachloride		N,N-Dimethyl Formamide		Additive TLVR				
				PPM	mg/m ³	PPM	mg/m ³	PPM	mg/m ³					
11/17/81 (Batch #3, T = 87°F, RH = 65%):														
P-1	785	13	NIOSH observer TWA	0.9	0.3	0.5	2.3	1.7	10.6	<0.2	<0.4	<0.1	<0.4	0.399
	773													
P-2	778	22	EPA operator TWA	2.1	7.3	0.3	1.4	3.6	23.0	<0.1	<0.2	0.3	0.9	0.801
	817													
S-1	811	15	Operator transferring waste from open container into inlet strainer	9.4	33.	0.4	2.0	16.	100.	<0.1	<0.3	<0.1	<0.3	0.927
	776			0.6	2.0									
S-2	794	15	Operator checking strainers and preparing system for start-up	19.	64.	<0.1	<0.3	2.6	16.	<0.1	<0.3	<0.1	<0.3	0.168
	777			0.4	1.3									
S-3	772	28	Operator obtaining bulk liquid waste sample from storage tank	<0.5	<1.8	<0.4	<1.8	1.1	7.2	<0.8	<1.8	<0.6	<1.8	0.055
	774													
11/18/81 (Batch #4, T = 87°F, RH = 65%):														
P-3	786	21	EPA operator TWA	0.7	2.4	0.6	2.9	1.0	6.7	<0.1	<0.2	<0.1	<0.2	0.267
	784													
P-4	775	23	NIOSH observer TWA	0.3	0.9	0.5	2.6	0.8	5.2	<0.1	<0.2	0.4	1.3	0.253
	779													
S-4	792	43	Operator connecting waste feed and vapor recovery lines, checking inlet strainer prior to storage tank filling	0.6	2.1	0.3	1.4	2.9	18.	<0.1	<0.1	<0.1	<0.1	0.152
	799													
S-5	C-1	12	Operator disconnecting feed and vapor lines, checking inlet strainer after tank filling	3.2	11.	0.7	3.2	1.0	6.4	<0.2	<0.4	<0.1	<0.4	0.360
	C-17	*		4.6	16.1	1.0	4.8	5.2	33.					
S-6	C-7	42	Worker assisting operator during connect procedure	0.1	0.2	0.1	0.5	0.4	2.6	<0.5	<0.1	<0.1	<0.1	0.023
	C-9	*		0.3	1.0									
S-7	C-6	13	Worker assisting operator during disconnect procedure	0.2	0.8	0.3	1.6	0.5	3.1	<0.2	<0.4	<0.1	<0.4	0.031
	C-4													
S-8	816	29	Stationary source sample placed next to centrifugal pump used for filling tank	0.1	0.34	<0.1	<0.2	0.2	1.4	<0.1	<0.2	<0.1	<0.2	0.010
	810	*		0.1	0.34									
11/19/81 (Batch #4):														
S-9	C-154	11	Operator obtaining bulk liquid waste sample from storage tank	4.3	15.	1.5	7.5	9.3	59.	0.2	0.5	0.2	0.5	0.504
	C-152													
Blank	798													
Blank	836													
Blank	745													
Blank	C-5													
Blank	C-22													
Blank	C-52													

*Indicates breakthrough

Table 4. Source sample exposure ranges and applicable standards.

	Detectable Exposure Range (ppm)	Standards PPM	
		OSHA Ceiling	TLV-STEL
Methylene chloride	0.1 - 19	1000	500
Chloroform	0.1 - 15	--	50
Carbon tetrachloride	0.2 - 16	25	20
Acetone	--	--	1250*
N,N-Dimethylformamide	0.3	--	20

*ACGIH intended change (1981) = 750 ppm

Table 5. Personal fullshift exposure ranges and applicable standards.

	Detectable Exposure Range (ppm)	Standards PPM		
		OSHA PEL	TLV-STEL	NIOSH*
Methylene chloride	0.3 - 2.1	500	100	75
Chloroform	0.3 - 0.6	50	10	10
Carbon tetrachloride	0.8 - 3.6	10	5	2
Acetone	--	1000	1000**	250
N,N-Dimethylformamide	0.4	10	10	--

* Recommended

**ACGIH intended change (1981) = 1000 ppm

DISCUSSION

The object of this study was to determine the effectiveness of the control measures being used at the San Juan cement demonstration in preventing worker exposure to the highly toxic hazardous waste supplemental fuels. Control effectiveness was to be reflected in the results of the industrial hygiene monitoring. Engineering controls and personal protective equipment were the control technologies used.

In general, low exposures were found to all substances monitored for. The potential for exposure was greatly reduced by using engineering controls. The vapor recycle line and the carbon bed in the waste storage/delivery system were effective vapor phase control measures. Some work procedures such as cleaning and inspecting in-line strainers, and connect/disconnect procedures during the filling of storage tanks, or some other incident, such as accidental spills, at times increased exposure potential. In these instances the use of protective equipment limited or prevented actual exposure. During this survey, the actual effectiveness of specific protective equipment items was not determined. However, observations indicated that this equipment was properly used.

The occurrence of possible increased exposure during normal work procedures and due to accidental spills indicates the importance of training in effective work practices for safe operation of systems containing hazardous wastes. Since this was a pilot operation performed by an outside contractor, a formal training program was not in place.

In order to fully evaluate the protection of worker health using air sampling data, some information concerning safe exposure limits must be known. In the case of exposure to complex and varying mixtures of organic compounds, additional knowledge of how these compounds may affect body systems (and hence exposure limits) when they are present concurrently is also desirable.

There are two alternate ways of dealing with the hazards from concurrent exposures. These are based on assumptions of additive or synergistic action.

Either one of these could be used to evaluate the potential exposures at the San Juan cement demonstration. Many of the body's systems could be affected additively by these materials. For example, acetone, ethanol, ethyl acetate, 2-propanol, toluene, chloroform, and methylene chloride all affect the central nervous system. Hexane and methane are both neurotoxic. All of the chlorinated compounds, toluene, and ethanol are hepatotoxins. On the other hand, a synergistic action could also take place. The toxic effect of carbon tetrachloride is potentiated (enhanced) by the presence of ethanol.^{2,3}

The American Conference of Governmental Industrial Hygienists has recommended guidelines to follow if additivity is assumed. Table 3 shows this calculation for the levels found in the present study. As seen, the cumulative TLV is not exceeded in any case for respiratory exposure. There is, however, a paucity of data concerning the synergistic action due to exposure to mixtures such as those encountered during the San Juan cement demonstration and how exposure limits are affected. Overall, there is insufficient knowledge of the specific mixtures and exposures at this plant to approach either alternative definitively.

CONCLUSION

This demonstration project was conducted by the EPA at the San Juan Cement Company to show whether various hazardous waste mixtures can be disposed of in an environmentally sound fashion by incineration during the manufacture of cement. These wastes may contain carcinogenic or suspected carcinogenic materials. The intent of this NIOSH survey was to determine if these hazardous waste mixtures could be handled in a safe fashion and to determine the effectiveness of the control technologies being used to prevent exposure to them.

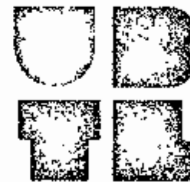
From the industrial hygiene monitoring results, the engineering controls used for vapor recovery seemed to be effective in suppressing vapor emissions resulting in low exposure levels. In the instances where exposure potential was increased, during the performance of certain tasks and when accidental spills occurred, the use of protective equipment can be effective. The questions of safe handling and minimizing exposure potential are best answered with training in effective work practices. If this type of operation is to continue, at this facility or at other locations, it is imperative that such training be policy.

REFERENCES

1. TLV's^R Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1981. American Conference of Governmental Industrial Hygienists.
2. Documentation of the Threshold Limit Values (4th Ed.). American Conference of Governmental Industrial Hygienists (1980).
3. Casarett and Doull's Toxicology. The Basic Science of Poisons. 2nd Ed. Edited by Doull, J., Klaassen, D. C., Amdur, M. O. MacMillan Publ Co., Inc., New York (1980).

APPENDIX A

February 5, 1982



RE: Seq. 3272-J
Gas Chromatography

UBTL
520 WAKARA WAY
SALT LAKE CITY,
UTAH 84108
801 581-8267

ANALYTICAL REPORT

SUBMITTED TO: M. Anaptos/M. Crandall

SUBMITTED BY: Ralph Meibos

REFERENCE DATA:

Analysis of: Methylene
Methyl Chloride, Chloroform, Carbon
Tetrachloride, Acetone and N,N-Di-
methyl Formamide

Project Identification No.: DPSE ECTB

Sequence No.: 3272-J

Sample(s): 32 Analyses: 160

UBTL Laboratory No: 82-00377 through 82-00408

The sample charcoal tubes numbered above were analyzed by gas chromatography using NIOSH Method P&CAM 127 with the following modifications:

Desorption Process	: 1 hour in 1 mL carbon disulfide containing 1 microliter/milliliter toluene as internal standard.
Gas Chromatograph	: Hewlett-Packard Model 5731 equipped with a flame ionization detector and accessories for capillary column use.
Column	: 60m x 0.32 mm I.D. fused silica WCOT coated internally with 0.25 μ m OV-351.
Oven Conditions	: 55 $^{\circ}$ C for 4 minutes programmed at 8 $^{\circ}$ C per minute to 130 $^{\circ}$ C for 2 minutes
Other	: Helium was used as the carrier in the split mode of operation with a split ratio of 20:1.

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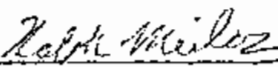
MINING
BIOMINERALS
CHEMISTRY

RESEARCH
DEVELOPMENT
ANALYSIS

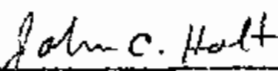
The detection limits for the requested analytes are listed below.

<u>Analytes</u>	<u>mg/sample</u>
Methylene	
Methyl-Chloride	0.01
Chloroform	0.01
Carbon Tetrachloride	0.01
Acetone	0.01
N,N-Dimethyl formamide	0.01

The results are tabulated on the following page(s).



Ralph Meibos



John C. Holt, CIH

cc: Donald D. Dollberg, Ph.D.



ANALYTICAL REPORT FORM

Date 5 Feb. 1982Agency Identification Number 3272-JCorporate/Agency Name NIOSH DPSE ECTBAddress 4676 Columbia Parkway R-5Cincinnati, Ohio 45226Attention M. Anaptos/M. Crandall Telephone 684 4347

Sampling Collection and Shipment

Sampling Site San Juan Cement Co. Date of Collection Nov 18, 1981Date Samples Received at UBTL January 12, 1982

Analysis

Method of Analysis GC-FIDDate(s) of Analysis 1-29 to 2-2-82

Analytical Results

Field Sample Number	UBTL Lab Number	Sample Type	Results mg/sample				
			METHYLENE CHLORIDE	CHLOROFORM	CARBON TETRACHLORIDE	ACETONE	N,N-DIMETHYL FORMAMIDE
[786]	82-00377	CT	83.0 0.05	119 0.06	154 0.14	58 <0.01	73 <0.01
784	82-00378		<0.01	<0.01	<0.01	<0.01	<0.01
[775]	82-00379		0.02	0.06	0.12	<0.01	0.03
779	82-00380		<0.01	<0.01	<0.01	<0.01	<0.01
798	82-00381		<0.01	<0.01	<0.01	<0.01	<0.01
C 5	82-00382		<0.01	<0.01	<0.01	<0.01	<0.01
836	82-00383		<0.01	<0.01	<0.01	<0.01	<0.01
745	82-00384		<0.01	<0.01	<0.01	<0.01	<0.01
[792]	82-00385		0.09	0.06	0.79	<0.01	<0.01
799	82-00386		0.21	<0.01	<0.01	<0.01	<0.01
C 22	82-00387	Blank	<0.01	<0.01	<0.01	<0.01	<0.01
[783]	82-00388	CT	0.04	0.03	0.14	<0.01	<0.01

Comments _____

Analyst J. MalveReviewer Ralph BarrowmanLaboratory Supervisor R. Barrowman JCA



ANALYTICAL REPORT FORM

Date 5 Feb. 1982Agency Identification Number 3272-J

Analytical Results

Field Sample Number	UBTL Lab Number	Sample Type	Results <i>mg/sample</i>				
			METHYLENE CHLORIDE	CHLOROFORM	CARBON TETRACHLORIDE	ACETONE	N,N-DIMETHYL FORMAMIDE
[773]	82-00389	CT	<0.01	<0.01	<0.01	<0.01	<0.01
[788]	82-00390		0.16	0.03	0.51	<0.01	0.02
[817]	82-00391		<0.01	<0.01	<0.01	<0.01	<0.01
[811]	82-00392		0.49	0.03	1.5	<0.01	<0.01
[776]	82-00393		0.03	<0.01	<0.01	<0.01	<0.01
[794]	82-00394		0.96	<0.01	0.24	<0.01	<0.01
[777]	82-00395		0.02	<0.01	<0.01	<0.01	<0.01
[772]	82-00396		<0.01	<0.01	0.02	<0.01	<0.01
[774]	82-00397		<0.01	<0.01	<0.01	<0.01	<0.01
[C 1]	82-00398		0.14	0.04	0.08	<0.01	<0.01
[C 27]	82-00399		0.20	0.06	0.41	<0.01	<0.01
[C 7]	82-00400		0.01	0.02	0.11	<0.01	<0.01
[C 9]	82-00401		0.04	<0.01	<0.01	<0.01	<0.01
[C 6]	82-00402		0.01	0.02	0.04	<0.01	<0.01
[C 4]	82-00403		<0.01	<0.01	<0.01	<0.01	<0.01
[816]	82-00404		0.01	<0.01	0.04	<0.01	<0.01
[810]	82-00405		0.01	<0.01	<0.01	<0.01	<0.01
[C 154]	82-00406		0.16	0.08	0.63	<0.01	<0.01
[C 152]	82-00407	V	0.01	<0.01	0.01	<0.01	<0.01
[C 52]	82-00408	Blank	<0.01	<0.01	<0.01	<0.01	<0.01
Limit of Detection			0.01	0.01	0.01	0.01	0.01

Comments _____