



Shell Oil Company
Interoffice Memorandum

SEPTEMBER 22, 1980

FROM: STAFF INDUSTRIAL HYGIENIST - S&IH/HS&E - SAN RAMON
TO: MANAGER, ANACORTES REFINERY
SUBJECT: PERSONNEL EXPOSURES DURING CATALYTIC CRACKER SHUTDOWN

As part of the continuing efforts to improve the employees' working environment and maintain compliance with appropriate regulations, one of the Corporate programs in progress is the investigation of potential health hazards associated with catalytic cracker shutdown work and effective methods to control them. A study was conducted the week of October 21-26, 1979, to evaluate potential exposures of personnel during the catalytic cracker shutdown. Personal monitoring was conducted for the following tasks:

- Removing coke from Reactor 2
- Removing catalyst from the Regenerator plenum
- Building the scaffold in the top of the Regenerator, 8th deck
- Air arc gouging in the secondary cyclones of Separator 1
- Air arc gouging to remove plenum skirt and welding on plenum in Regenerator
- Air arc gouging to remove bolts from Regenerator spider, 3rd deck
- Welding inside the Regenerator spider
- Welding hex metal in the Flue Gas Line on silencers, in West Seal Pot, and bottom of the East Damper.

These tasks were chosen because they were believed to represent an area for potential improvement from exposure due to the close proximity of the workers to the contaminants, the nature of the materials involved, and the difficulties of utilizing ventilation controls in close quarters.

Personnel worked an 8-hour shift the first day (Samples 1 - 3), and a 9½-hour shift the rest of the week. All samples were collected at the lapel (breathing zone) area. Respirators were used by all persons monitored, with the exception of four welders, as detailed at the bottom of Tables 2 and 3, Personnel Monitoring Results. Table 1 presents the exposure limits prescribed by the Washington Industrial Safety and Health Administration (WISHA), along with the Threshold Limit Values (TLVs) established by the American Conference of Governmental Industrial Hygienists (ACGIH). Table 4 summarizes the suggestions for improvements.

Regenerator

Two eductors, each with 11,200 cfm capacity, were installed in the dome during the 1976 shutdown to eliminate fumes in that area. The plenum—

DST-001257

eductor provides good ventilation for that area, and enhances the ventilation in the top of the regenerator by pulling air through the cyclones. This results in good general ventilation and visibility in the top area of the regenerator.

The laborer removing the caked catalyst from the plenum (Sample 2) did not encounter exposures exceeding the standards for the materials evaluated.

|| The carpenters building the peripheral scaffolding around the cyclones at the 8th deck level were confronted with heavy accumulations of fine catalyst on the cyclones and other surfaces. They encountered concentrations (Sample 3) exceeding the standards for Fe, Ni, V and Total Particulates. This loose catalyst probably accounted for a substantial portion of the Total Particulate found in the samples of welders working in that area later. As soon as the cyclones are accessible in each vessel, complete removal of catalyst buildup should be accomplished.

((Air arc gouging presents the greatest potential of exceeding the limits for Total Particulates and possibly Iron Oxide Fume. Of the six samples taken during air arc removal of the plenum skirt, one (Sample 12) exceeded the time-weighted average (TWA) standard for particulates based only on the 4-hour sample. Three others (Samples 7, 10 and 11) indicated the possibility of exceeding the limits. The highest Hexavalent Chromium value for this group was only 13% of the standard. The three samples for welding on the plenum with 308 stainless rod (containing 19% chromium) did not exceed the limits for Total Particulates or Chromium.

When the welder (air arcing or welding) is oriented between his work and the eductor, the fumes can be drawn directly into his breathing zone. One solution to this may be to shut off the eductor during this time to allow the fumes to exhaust towards the opposite eductor. Another may be the use of a temporary baffle in front of the eductor to divert the directional pull of the air.

Fresh air enters the regenerator through the 32 inch manway at the 8th deck and the 66 inch manway at the 3rd deck. A solid platform was installed at the 3½ deck level to protect workers in the bottom from debris falling from above. With only a small opening in the center of the platform for tugger cables, the air velocity in the lower work area was visually observed to be low. Sample 22 for the air arc removal of bolts from the outside of the spider exceeded the Total Particulate limits. An overlapping split platform may be considered, which may provide additional protection and allow unrestricted air flow. An exhaust with flexible duct fitted with a properly designed hood may be used in the area of the 3rd deck and, as work progresses, down into the lower cone to provide a strong directional exhaust for dusts and fumes.

Three samples were taken inside the spider while welding stainless doublers and inserts with 309 rod (containing 24% chromium). Sample 15 exceeded the Ceiling level for hexavalent chromium. Sample 18 was within limits. Sample 23 was high for Total Particulates for the time sampled, but due to the erratic work regime and short sampling time,

no estimate of a TWA could be made. Because of the tight working conditions in the spider header and one-way ventilation available, it would appear the most feasible control may be the use of a small high velocity exhaust hose with an efficiently designed capture hood which could be maintained in close proximity to the welding operation.

No. 2 Reactor

Three samples taken during the removal of coke in the bottom of the reactor (Samples 1, 4, and 8) showed results well below the standards for Benzene Soluble Particulates, Total Particulates, and Nickel. Respirators which filter both dusts and vapors should be used for this task to avoid breathing the hot hydrocarbon vapors. Blanking off the 3rd and 6th deck manways would produce a stronger flow of air through the bottom area for cooling and reducing vapor concentrations.

No. 1 Separator

Air arc gouging for removal of the chimney sleeves in the Secondary Cyclones (Samples 5 and 6) produced high Total Particulate concentrations, but did not exceed the limits for Hexavalent Chromium. An eductor with a flex hose used during Sample 6 to exhaust from beneath the cutting work was effective in reducing the fume concentration. Further reduction will be necessary and may be accomplished by exhausting air from the bottom of the dust hopper. A grating would be needed to serve as a work platform and to allow air movement, with a containment bin to trap the exhausted debris from the cutting work.

Flue Gas Line

Welding of hex metal on the first silencer baffle north of the slide valve with 309 rod (Sample 14) produced a Total Chromium concentration of 0.176 mg/m^3 . The welder was working on both sides of the baffle.

The laboratory reported considerable interference in the colorimetric analyses for Hexavalent Chromium from the iron present in the samples, and indicated these should be considered as maximum values. Sample 14 was analyzed as Total Chromium by the atomic absorption method, which had no interference. A study of welding fumes conducted at Texas A&M University, reported in the August, 1978 American Industrial Hygiene Association Journal, found about 73 percent of the Total Chromium content of the fume developed while welding with 308 stainless rods is present in the hexavalent state. The 309 rod used here contains more chromium, but applying the 73% factor to these results would indicate the Hexavalent Chromium concentration for Sample 14 would be 0.128 mg/m^3 or possibly more. The Nickel concentration for this sample was about 2% of the standard.

Similar welding on the third baffle (Sample 16) had low results. Welding was done on the south face only, and the stronger air flow was drawing the fumes away from the worker.

Ventilation was good in the area above the West Seal Pot where welding with 309 rod (Sample 17) produced low results. In the bottom of the

East Damper, however, the air flow was low and welding with 308 rod (Sample 20) produced Hexavalent Chromium results above the standard.

With more effective eductor use and temporary blanking of baffles or manways, effective exhaust of fumes away from the welders could be managed in the Silencer Baffle area. For contaminant control in the Damper section, the use of an eductor at the bottom nozzle of the Seal Pot and an open grating work platform to allow for downward air flow may be considered.

Summary

The results of this study further verify the information contained in the memo of General Manager, Manufacturing, September 7, 1979, on "Health Aspects of CCU Shutdowns". An Operations Task Force will review these study reports and issue guidelines for future shutdown work.

Adequate preparation of the vessels, scheduling of jobs with respect both to the available ventilation and prevention of cross contamination, and maximizing the effectiveness of the ventilation systems, will effectively provide the best environment and maintain compliance with governmental standards by affording adequate protection from contaminants with the possibility of increasing worker comfort and productivity.

RK Jones

R. K. Jones

RKJ / pb

Attachments

cc: Head Office - Operations Health and Safety - Manager
- Senior Industrial Hygienist
- HS&E - Corporate Medical - Occupational Health Surveillance - Director
- Safety and Industrial Hygiene - Manager
- S&IH - Industrial Hygiene Services - Manager
- Support Manager - A. J. Gonzalez

TABLE 1
EXPOSURE CRITERIA

<u>SUBSTANCE</u>	<u>PERMISSIBLE EXPOSURE LIMITS, mg/m³</u>	
	<u>WISHA</u>	<u>ACGIH TLV*</u>
Chromium: Chromic Acid, Chromates as CrO ₃ **	0.1C	0.05 as Cr
Soluble Chromic, Chromous Salts as Cr	0.5	0.5
Metal, Insoluble Salts as Cr	1.0	0.5
Coal Tar Pitch Volatiles: Benzene Soluble Fraction of Particulates	0.2	0.2
Iron Oxide: Fume, as Fe	10.0	5.0
Nickel: Metal, Insoluble Compounds as Ni	1.0	1.0
Soluble Compounds, as Ni	1.0	0.1
Total Particulates: Nuisance Dust	10.0	10.0
Vanadium (V ₂ O ₅): Dust, as V	0.5	0.5
as V ₂ O ₅		(0.05)
Fume, as V	0.05C	0.05C
as V ₂ O ₅		(0.05)

* American Conference of Governmental Industrial Hygienists, Threshold Limit Values as adopted 1980. Values appearing in "List of Intended Changes" shown in ().

** Both values listed are equivalent to 0.05 mg/m³ as chromium (hexavalent).

"C" designates the Ceiling Value.

TABLE 2
PERSONNEL MONITORING RESULTS

<u>Task</u>	<u>Sample No.</u>	<u>Time Min.</u>	<u>Total Particulate mg/m³</u>	<u>Benzene Soluble mg/m³</u>	<u>Fe mg/m³</u>	<u>Ni mg/m³</u>	<u>V mg/m³</u>
Removing coke from Reactor 2	1	394	-	0.06	-	-	-
	4	508	-	0.09	-	-	-
	8	496	1.71	-	-	0.004	-
Building scaffold in top of regenerator (1)	3	280	-	-	81.9	1.71	1.59
Removing catalyst from inside plenum	2	287	-	-	0.03	0.002	ND
(WISHA Standard)			(10.0)	(0.2)	(10.0)	(1.0)	(0.5)

(1) Sampled first carpenter 105 minutes and his relief 175 minutes.
All personnel wore 3M Brand 08710 Respirators.

*INCLUDE EXPOSURE
LIMITS, mg/m³ TO
THIS TABLE.
BBF*

TABLE 3
PERSONNEL MONITORING RESULTS

<u>Task</u>	<u>Sample No.</u>	<u>Time Min.</u>	<u>Total Particulate mg/m³</u>	<u>Hex. Cr mg/m³</u>	<u>Total Cr mg/m³</u>	<u>Ni mg/m³</u>
Air arcing chimney in Sec. Cyclones, Separator 1	5 (1)	45	173.0	0.0141		
	6	110	115.9	0.0046		
Air arc removing plenum skirt - regenerator	7	95	30.9	0.0042		
	9	105	2.38	0.0002		
	10	155	13.53	0.0046		
	11	151	30.8	0.0064		
	12	240	27.5	0.0059		
	13	240	4.21	0.0014		
ir arc removing bolts from spider-regenerator	22	323	18.2	0.0035		
Welding inside spider in regenerator	15	38	6.97	0.0921		
	18	304	2.22	0.0005		
	23	162	16.06	0.0008		
Welding on plenum-top of regenerator	19	405	2.72	0.0003		
	21	424	10.14	0.0013		
	24	156	2.65	0.0005		
Welding hex metal in Flue Gas Line: On Silencer	14	260	-	-	0.176 (2)	0.019
	16	90	4.82	0.0003		
In West Seal Pot in bottom of East Damper	17	340	1.56	0.0001		
	20	375	4.67	0.0733		
(WISHA Standard)			(10.0)	(0.05)		(1.0)

(1) Sampled first welder 32 minutes and relief for 13 minutes.

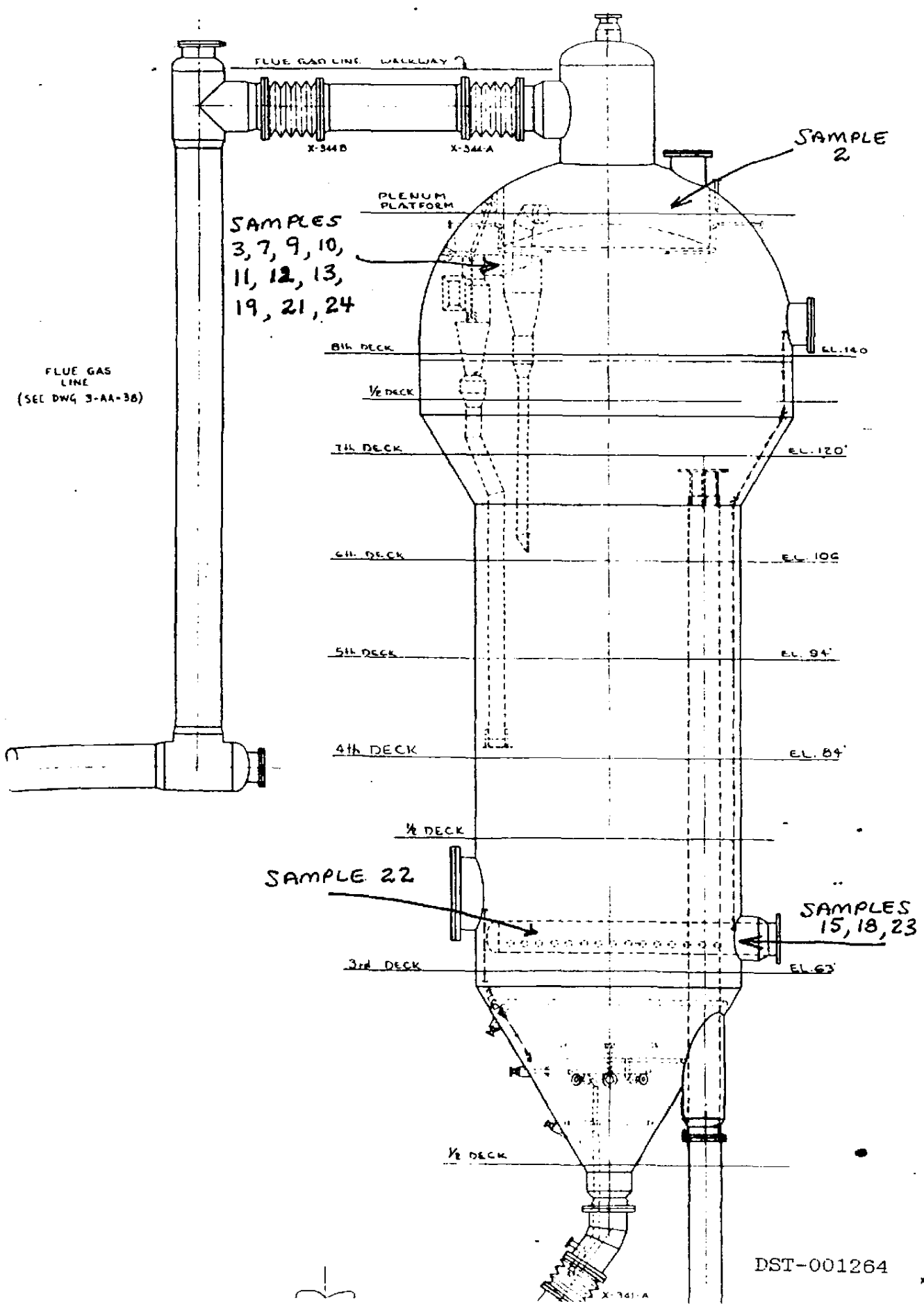
(2) Equivalent to about .128 mg/m³ as hexavalent chromium.

All personnel wore 3M Brand 9920 Respirators, except for welders in Samples 14, 20, 23 and 24 who used no respirator.

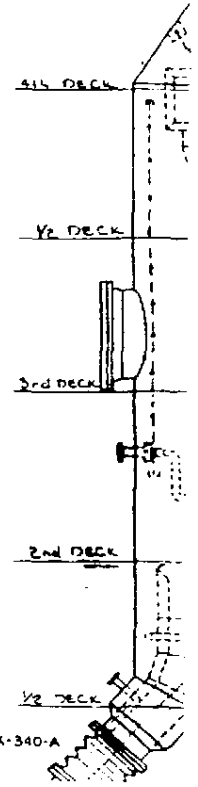
*INCLUDE EXPOSURE
LIMITS, mg/m³ TO
THIS TABLE.*

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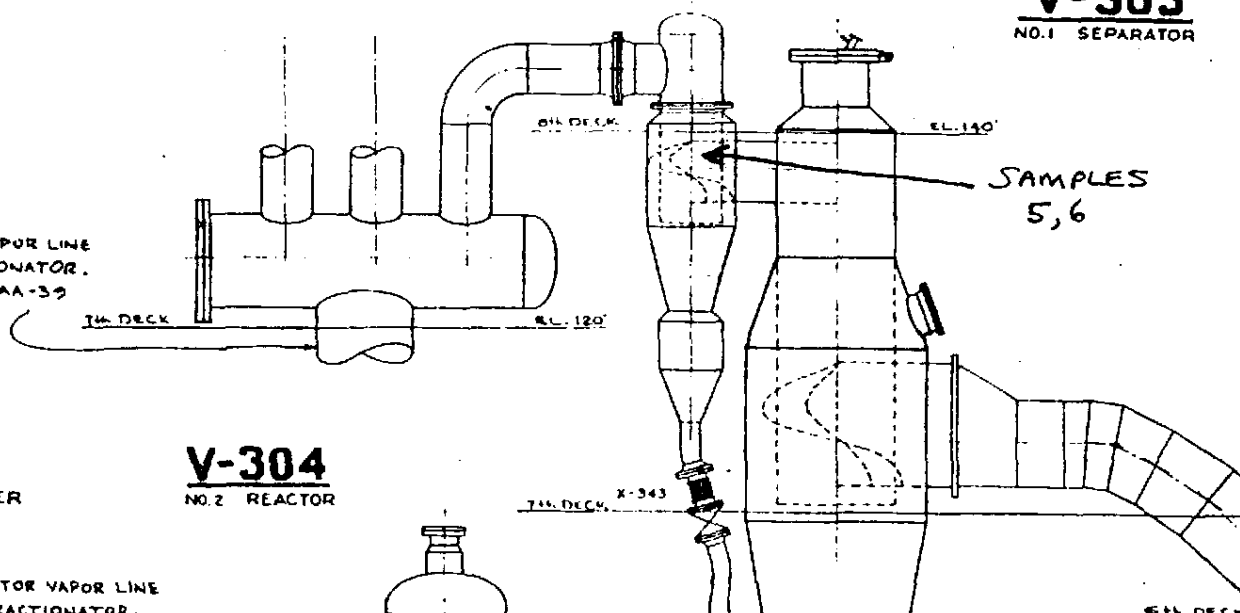
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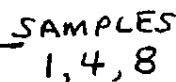
X-346



NO.1 SEPARATOR



V-304
NO. 2 REACTOR



C.O. BOILER #2

F-304

BLIND LOCATION

GASKET: 8005-0025
72-11/2" x 9 1/2" STUDS

BUTTERFLY VALVES

SAMPLE 17

DAMPER

SAMPLE 14

3 SILENCER BAFFLES

SAMPLE 20

SAMPLE 16

SLIDE VALVE

SEAL POT

V-309

DST-001266

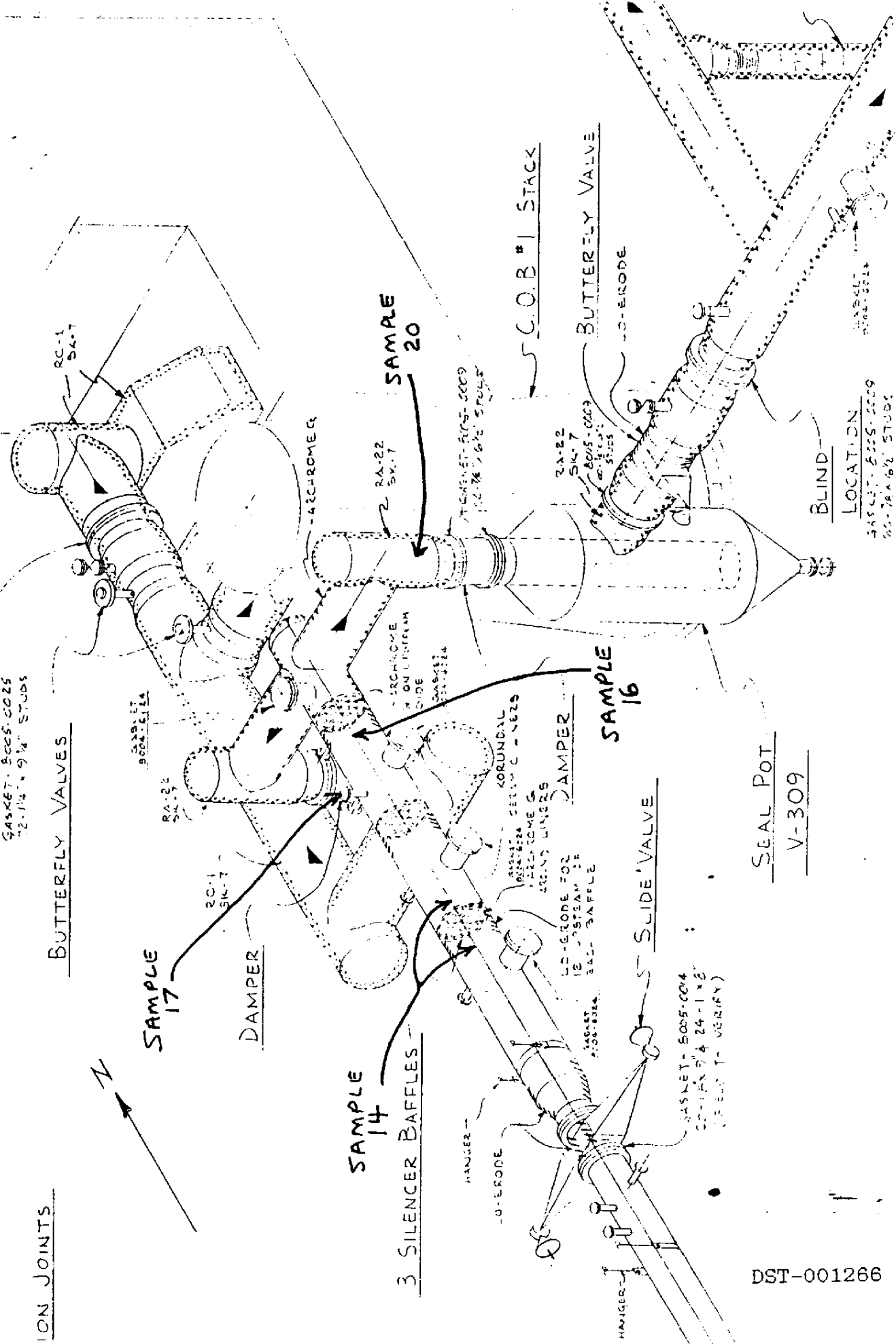


TABLE 4

SUMMARY OF RECOMMENDATIONS

Regenerator

- (1) Completely remove catalyst from vessels as early as possible to minimize exposures to the dust.
- (2) When welders must stand between the work and eductor, try to reduce the directional flow by modifying eductor speed or using a temporary baffle.
- (3) Consider a split platform over the lower work area to allow unrestricted air flow upward from the lower area.
- (4) Use a flexible dust exhaust in the cone below the 3rd deck for better control of dusts and fumes.
- (5) Use a small high velocity exhaust and hood inside the spider in close proximity to the welding.

No. 2 Reactor

- (6) Use combination dust and vapor respirators to prevent exposures to the hot hydrocarbons from the coke.
- (7) Consider blanking off the 3rd and 6th deck manways to produce stronger dilution ventilation in the bottom work area.

No. 1 Separator

- (8) Connect an exhaust system to the bottom of the dust hopper with appropriate traps to allow a strong downward air flow in the secondary cyclones during air arc gouging.

Flue Gas Line

- (9) Position eductors and temporarily blank baffles or manways to maintain the air flow across the welder, the work, and on to the outside in the Silencer baffle area.
- (10) Consider the use of an eductor at the bottom nozzle of the seal pot to provide better air flow in the Damper section.



Shell Oil Company
Interoffice Memorandum

SEPTEMBER 23, 1980

FROM: STAFF INDUSTRIAL HYGIENIST - S&IH/HS&E - SAN RAMON
TO: MANAGER, ANACORTES REFINERY
SUBJECT: CCU REPORT

Enclosed are two copies of the third draft of the CCU study report. Please call as soon as possible to let me know if further changes are necessary, or if we can proceed with final distribution.

R. K. Jones
R. K. Jones¹⁹

RKJ/pb

Enclosures