

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
CENTER FOR DISEASE CONTROL  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION  
REPORT NO. 79-8-584

STAUFFER CHEMICAL COMPANY  
SILVER BOW, MONTANA

APRIL 1979

I. TOXICITY DETERMINATION

A health hazard evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) at the Stauffer Chemical Company, Silver Bow, Montana, on December 19-21, 1978. At the time of this evaluation, breathing zone and general room air samples were taken on workers for phosphorus pentoxide ( $P_2O_5$ ), elemental phosphorus ( $P_4$ , yellow phosphorus), crystalline silica, total particulate, fluoride, and vanadium pentoxide ( $V_2O_5$ ). Concentrations of  $P_2O_5$  and crystalline silica exceeded the most recent evaluation criteria. Overexposure to  $P_2O_5$  were found in all samples that were taken. Crystalline silica overexposures were found in three out of four samples that were taken. All other environmental samples were well within the most recent evaluation criteria.

Stauffer has a very good respirator program which meets all the OSHA guidelines outlined in the General Industry Standards 1910.134. All workers are provided respirators and use them in areas where they are required.

Approximately 50 workers in areas of highest exposures to the contaminants mentioned above were interviewed. None of these workers had complaints. They were just curious as to the nature of the chemicals they were working with.

A potential health hazard did exist at the time of this survey due to excessive airborne concentrations of  $P_2O_5$  and respirable crystalline silica.

II. DISTRIBUTION AND AVAILABILITY

Copies of this determination report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available

through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office, at the Cincinnati address.

Copies of this report have been sent to:

1. Stauffer Chemical Company
2. Teamsters Local No. 2 - Butte
3. U.S. Department of Labor/OSHA - Region VIII
4. NIOSH - Region VIII

For the purpose of informing approximately 75-80 affected employees, a copy of this report shall be posted in a prominent place accessible to the employees for a period of 30 calendar days.

### III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

NIOSH received such a request from the Teamsters Local No. 2 in Butte, Montana, to evaluate potential exposures associated with the processing of ore and the production of elemental phosphorus.

### IV. HEALTH HAZARD EVALUATION

#### A. Process Evaluated

Phosphate ore enters the plant by way of a conveyor. It is dried in a kiln. The ore is then heated to about 1300 degrees Centigrade (C). At this stage elemental phosphorus nodules approximately 2-3 inches in diameter are formed in the ore. These nodules are drawn off, cooled, and stored in a silo. Coke and silica are added to the nodules. This mixture is electrically heated to about 5000 degrees C. Carbon monoxide and phosphorus gas are produced.  $P_4$  is collected by condensation. The liquid  $P_4$  is stored with water and an inert gas to prevent combustion. A flow diagram is included in the appendix.

#### B. Evaluation Design

There were approximately 50 workers on each shift in the specific area of this request. Workers who were receiving the

highest exposure (as prescribed by plant management and union officials) were monitored. A large number of the workers were interviewed, with questions directed at their work history and respiratory problems. Workers on the tap deck, roaster, burden bin, furnace, and all auxiliary areas were monitored.

C. Evaluation Methods

P<sub>2</sub>O<sub>5</sub> samples were collected on AA filters and analyzed according to NIOSH Method No. P&CAM 216. P<sub>4</sub> samples were collected on Tenax tubes and analyzed by flame photometry on a gas chromatograph according to NIOSH analytical Method No. S-334. Fluoride samples were collected on 37 mm filters using vacuum pumps operated at 1.5 liters per minute. These samples were analyzed according to NIOSH Method No. P&CAM 212. Crystalline silica samples were collected on 37 mm filters using cyclones and vacuum pumps operated at 1.7 liters per minute. These samples were analyzed by NIOSH Method No. P&CAM 109. Vanadium pentoxide samples were collected on 37 mm filters at 1.5 liters per minute and analyzed according to NIOSH Method No. P&CAM 173.

D. Criteria for Assessing Workroom Concentrations of Air Contaminants

Four sources of criteria are generally used to assess workroom concentrations of air contaminants: (1) NIOSH criteria for recommended standards; (2) recommended Threshold Limit Values (TLVs) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists (ACGIH), 1977; (3) Occupational Safety and Health Administration (OSHA) standards (29 CFR 2920), January 1976; and (4) American Industrial Hygiene Association (AIHA) Hygienic Guide Series. NIOSH criteria and ACGIH TLVs represent the most recent and relevant recommendations and are given prominence in this evaluation.

<u>Substances</u>	NIOSH Criteria for Recommended Standard	Permissible Exposures 8-Hour Time-Weighted Exposure Basis (mg/M <sup>3</sup> )		
		ACGIH TLV	Current OSHA Standard	AIHA Hygienic Guide
P <sub>2</sub> O <sub>5</sub> .....	---	---	---	1.0*
P <sub>4</sub> .....	---	0.1	0.1	---
Crystalline Silica..... (respirable)	0.05	10 mg/M % Respirable Quartz + 2		---
Total Particulate.....	---	10.0	15.0	---
Fluoride.....	---	2.5	2.5	---
Vanadium Pentoxide.....	---	0.5	0.5	---

\* No OSHA or ACGIH criteria exists; therefore, this evaluation criteria was the best available and corresponds to Patty's Volume II, Second Revised Edition, pp. 1172-1180.

mg/M<sup>3</sup> = milligrams of substance per cubic meter of air

Occupational health standards are established at levels designed to protect individuals occupationally exposed to toxic substances on an 8-hour per day, 40-hour per week basis over a normal working lifetime.

E. Toxicology

Crystalline Silica -- exposures at levels above the recommended criteria can produce a fibrotic condition of the lungs (silicosis). This is a disabling disease that can lead to permanent disability and death. Maintaining a worker's exposure below 0.05 mg/M<sup>3</sup> should prevent any occupational disease.

Total Particulate -- exposures should be controlled so that workers are not exposed to over 10 mg/M<sup>3</sup>. Respirators should be worn when levels exceed this concentration.

Phosphorus Pentoxide -- moderate for both acute and chronic exposures. Phosphoric anhydride is a local irritant and a very strong dehydrating agent. With moisture it forms phosphoric

or sulfuric acid. Very high concentrations of the anhydride will cause violent coughing, although those exposed regularly to the industrial fume apparently become acclimated to some degree. No evidence of systemic poisoning from either acute or chronic exposure. (Reference 1)

Elemental Phosphorus -- may be toxic by inhalation, ingestion, and skin contact.  $P_4$  causes fatty degeneration of the liver and kidneys, and erosion of gastrointestinal tract. Of greatest importance is its ability to cause osteoporosis, especially of mandible (phossyjaw).  $P_4$  also causes damage to the bone marrow. Maintaining occupational exposures below  $0.1 \text{ mg/M}^3$  should prevent the workers from any of these disabling conditions. (Reference 2)

Fluoride -- is toxic by inhalation and ingestion and may cause nephritis, osteosclerosis, and pulmonary fibrosis. After long chronic exposure to high levels of fluoride, one might develop "fluorosis" (hypermineralization of the skeleton, calcification of ligaments, immobilization of joints). Maintaining levels below  $2.5 \text{ mg/M}^3$  should prevent any adverse health effects. (Reference 3)

Vanadium Pentoxide -- Vanadium is unquestionably poisonous to all animals in any but very small doses, no matter how it is administered, according to Hudson (Reference 4). The pentavalent compounds, such as  $V_2O_5$  and vanadates, are more toxic than other forms. A lethal dose by intravenous administration to the rabbit is about  $1.5 \text{ mg } V_2O_5/\text{kg}$ . Rats taking 25 ppm in the diet show early signs of poisoning. Vanadium pentoxide dust at concentrations of  $70 \text{ mg/M}^3$  is fatal to animals within a few hours.

When inhaled, the chief effects of vanadium pentoxide are on the respiratory passages. Tracheitis, bronchitis, emphysema, pulmonary edema, or bronchial pneumonia may be observed, but no specific chronic lung lesions have been described (Reference 4).

Sjoberg (Reference 5) reported a number of cases, most of them mild, among workers in a vanadium refinery. Concentrations ranged up to  $12 \text{ mg/M}^3$  of  $V_2O_5$  at first, but later exposures were reduced. He later (Reference 6) described seven cases of respiratory irritation among boiler cleaners. Concentrations in the air ranged from 2 to  $85 \text{ mg/M}^3$ .

Williams (Reference 7) reported vanadium intoxication in eight men who cleaned boilers. Air tests indicated concentrations, calculated as  $V_2O_5$ , from 30 to  $104 \text{ mg/M}^3$ ; apparently respirators were worn to some extent. Vintinner and co-workers (Reference 8) reported a study of workers engaged in mining and

processing vanadium ores. There was no systemic poisoning, but many workers suffered from local (respiratory) effects. Concentrations of vanadium (as  $V_2O_5$ ) ranged up to  $3 \text{ mg/M}^3$ , in one area, and to over  $100 \text{ mg/M}^3$  in another.

McTurk et al. (Reference 9) reported that workers exposed intermittently (once or twice a month) at  $99 \text{ mg/M}^3$  of  $V_2O_5$  showed no evidence of intoxication. Gauze filters were worn. Gulko (Reference 10) referred to eye and bronchial irritation from exposures at  $0.5$  to  $2.2 \text{ mg/M}^3$ . Lewis (Reference 11) noted a higher incidence of respiratory symptoms in workers exposed generally at concentrations between  $0.2$  and  $0.5 \text{ mg/M}^3$  than in controls.

Hudson (Reference 4) stated that workers, exposed at concentrations averaging  $0.25 \text{ mg } V_2O_5/\text{M}^3$  needed respiratory protection to prevent signs and symptoms such as green tongue, metallic taste, throat irritation and cough. These men worked chiefly with  $V_2O_5$  and ammonium metavanadate.

Threshold limits of  $0.5 \text{ mg/M}^3$  air for vanadium pentoxide dust, and  $0.1 \text{ mg/M}^3$  for the pentoxide as a fume, were suggested by Roshchin (Reference 12) on the basis of limited animal studies made in reference to animal exposures. These values were subsequently incorporated in the USSR list of permissible concentrations. Extensive studies by Stokinger and co-workers with animals, using vanadium pentoxide dust at the recommended limit at respirable particule sizes, substantiated the recommendation of Roschin for  $V_2O_5$  dust with regard to lack of systemic or localized effect in the lung (Reference 13).

#### F. Environmental Results and Discussion

Results of environmental samples showed that workers were exposed to excessive levels of phosphorus pentoxide and crystalline silica. About 50 workers were interviewed. Examination of these interviews showed that workers had no complaints. It should be noted that these interviews were directed towards overexposures to  $P_4$  and  $P_2O_5$  and other contaminants listed in this report.

Results of all environmental samples may be reviewed in Tables I through V. This company employes a dentist who visits the plant one day a week. The dentist was interviewed; according to his data, dental problems are almost non-existent. He has not seen a case of extreme  $P_4$  poisoning (phossyjaw) in many years. The workers that were interviewed also admitted that their dental hygiene was monitored very closely.

G. Conclusions

Results of environmental data illustrate that a potential health hazard existed during this evaluation. It should be noted that workers who are exposed to phosphorus pentoxide and crystalline silica are protected by a very adequate respiratory program which meets all OSHA requirements under 1910.134. In the area where high crystalline silica levels were found, the worker has a dust free booth to stand in and a respirator to wear when he enters the hazardous environment. Workers exposed to  $P_2O_5$  have no other protection except respirators.

V. RECOMMENDATIONS

1. The current respirator program should be maintained since it is excellent.
2. All workers should be clean shaven, since it is inevitable that it will become a problem where respirators are required. It is impossible to get an adequate fit over facial hair. Therefore, every worker should be clean shaven just prior to his tour of duty.
3. Workers should be briefed on the hazards of working with  $P_2O_5$ , crystalline silica, elemental phosphorus, fluoride, total particulate, and vanadium pentoxide.
4. A continuing effort should be made to improve local and general ventilation throughout the plant.

VI. REFERENCES

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TABLE I

Breathing Zone and General Room Air Concentrations of  
Phosphorus Pentoxide (P<sub>2</sub>O<sub>5</sub>)

Stauffer Chemical Company  
Silver Bow, Montana

December 19, 1978

<u>Sample Number</u>	<u>Location</u>	<u>Job Classification</u>	<u>Time of Sampling</u>	<u>mg/M<sup>3</sup> P<sub>2</sub>O<sub>5</sub></u>
48	Tap Deck	Tapper Helper	8:50 AM - 3:20 PM	3.4
45	Tap Deck	Tapper	8:45 AM - 3:20 PM	3.0
29	Tap Deck	Tapper	8:46 AM - 3:20 PM	2.2
43	Tap Deck	Tapper	8:20 AM - 3:06 PM	2.6
37	Tap Deck	Lead Man	8:25 AM - 3:09 PM	9.2
40	Roaster	Operator	8:05 AM - 3:12 PM	1.7
28	Furnace	1st Helper	8:15 AM - 3:06 PM	1.9
46	All Over Plant	Painter	8:17 AM - 3:30 PM	3.1
42	Furnace	General Room	8:12 AM - 2:20 PM	4.2

EVALUATION CRITERIA

1.0

LABORATORY LIMIT OF DETECTION mg/sample

0.004

Workers wore respirators when working in contaminated air.

TABLE II

Breathing Zone Air Concentrations of  
Elemental Phosphorus (P<sub>4</sub>)

Stauffer Chemical Company  
Silver Bow, Montana

December 19, 1978

<u>Sample Number</u>	<u>Location</u>	<u>Job Classification</u>	<u>Time of Sampling</u>	<u>mg/M<sup>3</sup> P<sub>4</sub></u>
P1	Phosphorus	P <sub>4</sub> Helper	8:12 AM - 1:30 PM	0.06
P2	Phosphorus	P <sub>4</sub> Operator	8:11 AM - 1:30 PM	0.07
P3	Phosphorus	P <sub>4</sub> Operator	8:10 AM - 3:00 PM	0.04
P4	Phosphorus	General Room	8:10 AM - 2:00 PM	0.03
P5	Phosphorus	P <sub>4</sub> Helper	8:08 AM - 2:00 PM	*

EVALUATION CRITERIA	1.0
LABORATORY LIMIT OF DETECTION ug/sample	0.07

\* = below laboratory limit of detection

TABLE III

Breathing Zone and General Room Air Concentrations of  
Crystalline Silica and Total Particulate

Stauffer Chemical Company  
Silver Bow, Montana

December 19-20, 1978

Sample Number	Location	Job Classification	Time of Sampling	mg/M <sup>3</sup>	
				Crystalline Silica	Total Particulate
3363	Burden Bin	Operator	8:30 AM - 3:00 PM	0.09	1.7
3353	Burden Bin	General Room	8:35 AM - 3:00 PM	0.183	2.1
3421	Burden Bin	General Room	8:30 AM - 3:25 PM	*	0.50
3402	Burden Bin	Operator	8:34 AM - 3:25 PM	0.14	3.0
EVALUATION CRITERIA				0.05	5.0
LABORATORY LIMIT OF DETECTION mg/sample				0.03	0.01

\* = below laboratory limit of detection

TABLE IV

Breathing Zone and General Room Air Concentrations of  
Fluoride

Stauffer Chemical Company  
Silver Bow, Montana

December 19-20, 1978

<u>Sample Number</u>	<u>Location</u>	<u>Job Classification</u>	<u>Time of Sampling</u>	<u>mg/M<sup>3</sup> Fluoride</u>
33	Kiln	General Room	8:55 AM - 3:10 PM	0.007
30	Kiln	Kiln Operator	8:48 AM - 3:16 PM	0.05
27	Kiln	Kiln Burner	8:45 AM - 3:15 PM	0.02
49	Kiln	Helper	8:54 AM - 3:10 PM	0.02

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EVALUATION CRITERIA	2.5
LABORATORY LIMIT OF DETECTION mg/sample	0.002

TABLE V

Breathing Zone Air Concentrations of  
Vanadium Pentoxide ( $V_2O_5$ )

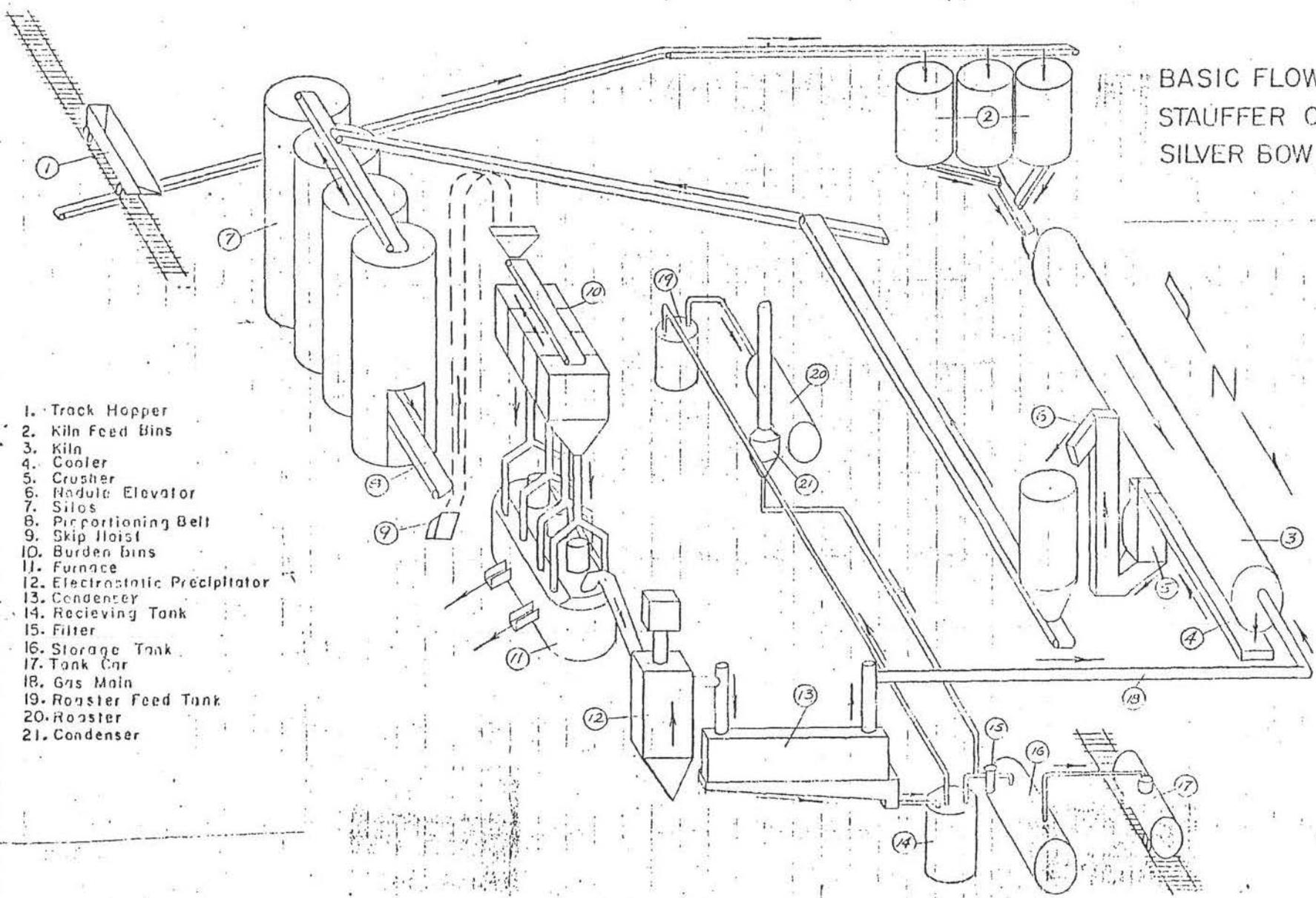
Stauffer Chemical Company  
Silver Bow, Montana

December 19-20, 1978

Sample Number	Location	Job Classification	Time of Sampling	mg/M <sup>3</sup> V <sub>2</sub> O <sub>5</sub>
47	Roaster	Roaster Operator	8:20 AM - 3:30 PM	*
35	Furnace	Precipitator operator	8:40 AM - 3:25 PM	*
EVALUATION CRITERIA				0.05
LABORATORY LIMIT OF DETECTION mg/sample				0.011

\* = below laboratory limit of detection

BASIC FLOW DIAGRAM  
 STAUFFER CHEMICAL CO.  
 SILVER BOW, MONTANA



1. Track Hopper
2. Kiln Feed Bins
3. Kiln
4. Cooler
5. Crusher
6. Radula Elevator
7. Silos
8. Proportioning Belt
9. Skip Hoist
10. Burden bins
11. Furnace
12. Electrostatic Precipitator
13. Condenser
14. Receiving Tank
15. Filter
16. Storage Tank
17. Tank Car
18. Gas Main
19. Roaster Feed Tank
20. Roaster
21. Condenser